

# THE CHEMISTRY OF WOOD

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## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

## *GENERAL INTRODUCTION*

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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## Foreword

The following work is the product of the joint efforts of both authors. Parts I, II and III were written by Louis E. Wise. Parts IV and V were written by L. F. Hawley. However, the entire manuscript has been gone over critically by both authors, who thus share a joint responsibility.

We wish to thank the members of the staff of the Forest Products Laboratory for their helpful suggestions and criticisms. Special thanks are due, also, to Dr Harry P. Brown, Professor of Wood Technology at the New York State College of Forestry, for his valued advice, constructive criticism, and active help in the preparation of our manuscript.

L. F. H.  
L. E. W.



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## PART I

### INTRODUCTION

A brief statement regarding the aim of this book, its subject and its applications would seem in place.

To the best of our knowledge, no attempt has hitherto been made to bring together within the compass of a single book, data pertaining solely to the chemistry of wood. Our own attempt to develop a monograph on this subject therefore resembles a pioneering adventure. We have worked unhampered by trails or precedents, and if our volume contains (as it may) numerous errors of commission and omission, we feel that at least it serves to summarize the outstanding contributions on a subject that has received but scant attention in the United States.

The results of purely scientific investigations on wood chemistry have been stressed and we have attempted to point out the many gaps and loopholes in our present knowledge. This has led us occasionally to indicate what new avenues of investigation might profitably be opened in the future. In the case of moot questions, we have attempted to present the experimental data and to discuss the viewpoints of the various investigators open-mindedly. On the other hand, we have consistently attempted to differentiate between *speculation* and *investigation*.

Every effort has been made to show that the chemistry of wood is a live and rapidly growing field of investigation and that researches in this field are of fundamental importance to biology and to industry. However, we have made no attempt to write chapters on the practical phases of chemical wood utilization and the reader must not look for detailed descriptions of industrial processes. Our task has been approached in what we trust is a critical but constructive spirit. While we are glad to acknowledge our indebtedness to such standard works as Czapek's "Biochemie der Pflanzen" and Schwalbe's "Chemie der Cellulose" (and to a number of other books referred to in appropriate places in the text), most of our material has been culled directly from the original sources in the literature. Not infrequently we have given, in detail, methods and data accumulated during the past 12 years by the United States Forest Products Laboratory.

Most of the sources referred to above were reviewed critically before they were summarized and incorporated into the monograph. It is a com-

mon and very human failing among certain investigators to draw sweeping conclusions on the basis of very meagre experimental data. In the field of forest products, some excellent chemists and technologists have occasionally erred in this way. Hence we have been led to examine critically the experimental parts of numerous articles before accepting the author's conclusions.

The difficulties in presenting some of our material in coherent and lucid form at first appeared baffling and almost insurmountable. As an example, the two chapters on *lignin* were outlined and reoutlined, written and revised several times before they even approximated a satisfactory exposition of a subject that has been befogged in speculation and bandied to and fro in an endless series of polemics and debates. We present them, now, with a certain degree of temerity but without apology. We have tried to make our monograph useful, suggestive, and stimulating, rather than all inclusive. We deliberately omitted many references to articles on wood chemistry which were not germane to the subject or which presented the opinions of the author rather than his experimental results.

\* \* \* \* \*

It is not an easy matter to define, delimit, or even to explain the term "woody plant." The dendrologist, whose function it is to study the taxonomy of woody plants, has realized this and has approached his task with the proper care and mental reservations.<sup>1</sup>

Those woody plants which are of distinct economic value form a part of the plant *sub-kingdom* known as the spermatophytes. These spermatophytes include all seed plants and the sub-kingdom is divided further into two classes:

1. The Gymnosperms
2. The Angiosperms.

The gymnosperms have seeds which are not borne in an ovary. They include the coniferous trees (the softwoods). The angiosperms have seeds which are enclosed in an ovary. They include the deciduous trees of the temperate zones (the hardwoods). It is not within our sphere to discuss the use of the terms "softwoods" and "hardwoods" further than to say that the names do not always adequately suggest the physical properties of the wood of these trees.

Woody plants live on perennially. Furthermore they possess specialized conducting tissue (also known as vascular tissue). The woody part of this tissue (xylem), as it matures, undergoes certain physicochemical

<sup>1</sup>Cf. H. P. Brown, "Trees of New York State, Native and Naturalized," Technical Publication of the New York State College of Forestry No. 15, pp. 9-20 (1921), from which a part of this material has been taken. Our thanks are due to Dr. Brown for a very careful reading of this portion of the introduction.

changes that have been grouped together under the obscure, collective term "lignification," of which we shall have more to say in Chapter 3 of Part II. The process of lignification causes cell walls to become strengthened and hardened and all woody tissues become more or less lignified, soon after the cells have reached their ultimate size. While lignification is not limited to woody plants, these plants possess more lignified tissue than do herbaceous plants and hence may be characterized in this way.

Were it not for this process of lignification, the woody plant would be unable to support an aerial axis (or stem) which grows and persists from year to year. In trees this stem is generally spoken of as the bole or the trunk. We can think of this bole as being made up of three parts which are unlike: the pith, the wood and the bark. The pith forms a narrow cylinder of soft tissue running vertically through the central part of the stem. The outside of the stem is covered with bark, and between pith and bark lies the wood (or xylem).<sup>2</sup>

Through the activity of a growing layer (known as the cambium) typical woody plants have the means of thickening their stems. The cambium separates the last layer of wood from the bark of the tree and gives rise to new bark and to new wood annually. The woody tissue arising from the cambium is termed *secondary wood*, and this is (from the technological standpoint) the most important part of the stem.<sup>3</sup> It is the chemistry of this secondary wood that forms the subject matter of this book.

If we should make a cross-section of the bole of a tree (grown in a temperate region) we would find the formation of secondary wood indicated by a series of concentric bands (usually known as *annual rings*). Each individual ring consists of two parts (1) an inner part toward the pith, termed the *springwood*, and (2) an outer part toward the bark, known as the *summerwood*.<sup>4</sup> The springwood (or "early wood") is the lighter, and is usually made up of thin walled cells with relatively large openings. The summerwood (the late wood) frequently has a denser structure with thick walled cells and much smaller openings.

During the growth of the tree the peripheral layers of the wood (i.e. those nearest the cambium) contain a large proportion of living cells and these layers (since the movement of sap takes place within them) are

<sup>2</sup>Cf. C. J. Record, "Economic Woods of the U. S.", 2nd Edition, John Wiley & Sons (1919), Part I. For a more complete description, cf. Eames and MacDaniels "Introduction to Plant Anatomy," McGraw-Hill (1925), Chapter I.

<sup>3</sup>In trees the *primary wood* is contiguous to the pith and is so restricted as to be negligible.

<sup>4</sup>We have made no attempt to give the distinctions between the springwood and summerwood of gymnosperms and the characteristic differences between early and late wood in the ring-porous and diffuse porous angiosperms. For such descriptions cf. Record's "Economic Woods of the U. S.", pp. 40-41, and Koehler, "Properties and Uses of Wood," pp. 8 and 15, McGraw-Hill Book Co. (1924).

grouped together under the convenient term *sapwood*. The wood nearer the pith, which has lost its physiological activity and performs a purely mechanical function, is termed *heartwood*. This is often darker and heavier than sapwood and not infrequently contains an accumulation of extraneous substances. There is no evidence of increased lignification in passing from sapwood to heartwood. (This is substantiated in the main by analytical data in Part III, Chapter 6.)

Wood is by no means a homogeneous substance. It has a fibrous structure and is made up of cells which in cross-section present a characteristic porous appearance. Interdependence of these cells (at least originally) is indicated by the fact that they have a common medial layer (known as the middle lamella) upon which secondary layers are deposited, and also through the presence of pits or thin places in their walls. The middle lamella may be looked upon as a cementing layer which binds together adjoining cells. The chemistry of the middle lamella has recently been reinvestigated.<sup>5</sup> Each cell has, as components of the secondary layer of the cell wall, substances that have never been clearly defined but which include cellulose, polysaccharides other than cellulose, and lignin. These components will be discussed from the chemical standpoint in Chapters 1-4 of Part II. The cell wall encloses a *lumen* or *central cavity* which usually contains extraneous material, since this cavity functions in the transportation of food and water, in the storage of food, etc.<sup>6</sup>

Woody tissue includes different types of cells which the botanists term *elements*. Two general types exist:

- (1) The prosenchymatous elements.
- (2) The parenchymatous elements.

The prosenchymatous elements function in part in conducting water and dilute aqueous solutions, in part in imparting strength and toughness to the wood. The parenchymatous elements aid largely in the conduction and storage of carbohydrate food materials elaborated by the plant.<sup>7</sup> The wood of angiosperms is more heterogeneous than that of the gymnosperms.

We have mentioned this heterogeneity of wood since (in the case of hardwoods) the chemist has worked almost exclusively with wood substance in its entirety. He has not been able to dissect out and examine chemically elements of a given type. In other words, he knows very little about the chemistry of the respective (botanical) elements as found in woods.<sup>8</sup> He has an easier problem perhaps with the softwoods which

<sup>5</sup>Cf. Chapters 2 and 3 of Part II

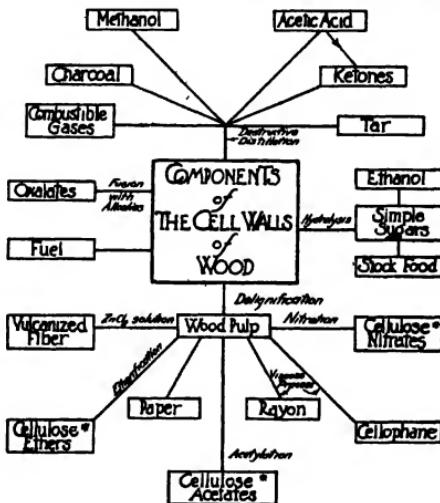
<sup>6</sup>Extraneous substances of wood are discussed and defined in Chapter 5, Part II.

<sup>7</sup>For a description of the microscopic structure of wood, cf. Chapter 1, Part V.

<sup>8</sup>Some sixty years ago, Fremy, a French chemist, made the attempt to separate and examine these various (botanical) elements, but his results were unsatisfactory. Cf. Chapter 3, Part II.

possess fewer kinds of elements and which may be chemically treated so as to remove nearly everything except the tracheids (prosenchymatous elements). However, here too we have no comparative data on the chemistry of coniferous tracheids in comparison with that of ray or longitudinal parenchyma (parenchymatous elements). The reader must bear this in mind when he approaches the study of the chemistry of wood.

One other fact may be emphasized. In the present volume we are dealing with the chemistry of wood, *a product that has already been elaborated*.



### CHEMICAL UTILIZATION OF COMPONENTS OF THE CELL WALLS OF WOOD

\* Cotton is normally used but wood cellulose may be employed.

FIG. 1.

rated by the plant. Our subject, then, is static, not dynamic. We shall have little to say about the mechanism of growth nor shall we discuss in much detail the synthesis of the various components of wood. While we realize the fundamental importance of the field from which we are deliberately turning aside, we feel justified by the knowledge that this is unexplored territory. Synthetic enzyme reactions dealing with the formation of substances in the cell walls of plants have not been studied.

Although we have disclaimed any attempt to discuss the chemical utilization of wood from the standpoint of the technologist, it appears quite

proper to make a passing reference to those chemical industries (present or potential) which depend on wood, wholly or in part, for their raw material.

Destructive distillation<sup>9</sup> is used in converting hardwoods like beech, maple and birch into methanol, acetic acid, acetone, charcoal, and tar. While the industrial manufacturer of methanol, up to two years ago, used wood as his sole raw material, synthetic methanol can now be prepared from carbon monoxide and hydrogen reacting under high pressure in contact with suitable catalysts.<sup>10</sup> In 1924, 48 gallons of methanol were imported into the United States. During the first ten months of 1925, the imports totalled very nearly 425,000 gallons.<sup>11</sup> The full effect of synthetic methanol production on the future of the wood distillation industry is still a matter of conjecture.

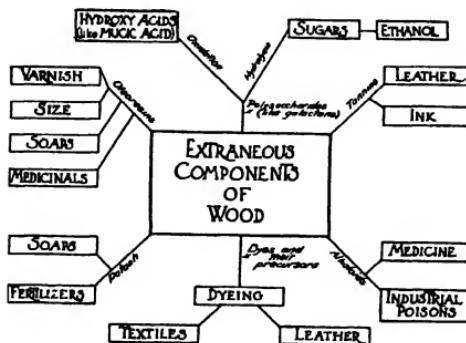
Formerly the industrial preparation of oxalates depended almost entirely on the fusion of wood waste with alkali.<sup>12</sup> The more modern commercial method, however, involves the dehydrogenation of sodium formate with the formation of sodium oxalate.

The acid hydrolysis of wood gives rise to simple sugars, which permit the use of partially hydrolyzed wood as a cattle food and in the production of ethanol.<sup>13</sup> These industrial applications have not been exploited to any great extent in the United States.

The delignification of wood,<sup>14</sup> however, plays an enormous rôle in the production of chemical pulp. Wood pulp forms an important raw material of the paper and rayon (artificial silk) industries and promises to become increasingly important in the production of cellulose nitrates, acetates and ethers, and in the formation of specialized products like vulcanized fiber, cellulose wool ("snialf") and hydrated cellulose films ("cellophane"). In some industries the use of wood pulp runs parallel to that of cotton, the relative amounts used as raw material depending on economic conditions in the country in which the production is being carried out and on the availability of the raw material. As an example—in Germany during the war a high grade of wood pulp was used in the manufacture of explosives. In the United States cotton formed the only important raw material used in the production of the higher cellulose nitrates.

The chemical changes, the commercial aspects of which are briefly referred to above, deal largely with the alterations taking place in the *cell-walls* of wood. The components of wood which are not properly a part

of the cell wall also play a rôle in industry. Such components include the tannins, resins, dyes (or their precursors), essential oils, gums, alkaloids, etc., all of which must be considered chemical products of the tree. As a specific example of the utilization of such products, we might refer to long-



### INDUSTRIAL SIGNIFICANCE OF EXTRANEous COMPONENTS (EXTRACTIVES) OF WOOD

FIG. 2.

leaf pine wood which when extracted and distilled with steam, yields wood rosin and wood turpentine.<sup>15</sup>

A number of extraneous substances are found in tropical woods and some of them serve to characterize the wood. The chemical exploration of these compounds which has just begun, should furnish a rich and fascinating field for the investigator interested in applied organic chemistry.

<sup>15</sup> Cf. Chapter 5, Part II.



# PART II

## CHEMICAL COMPONENTS OF WOOD

### Chapter I

#### Cellulose, the Principal Component of the Cell Wall

Ever since Payen's discovery that woody tissue contained a resistant, insoluble polysaccharide ( $C_6H_{10}O_5$ )<sub>n</sub>,—"cellulose"<sup>1</sup>—this substance has been recognized as the characteristic component of the cell wall. Yet the use of the term "substance" might be challenged. Cross and Bevan, on the first page of their monograph "Cellulose," state: "There are, as might be expected, many varieties of cellulose and the term must be taken as denoting a chemical group." They continue by describing this group of substances as insoluble in the "simple solvents, generally, but variably resistant to oxidation and hydrolysis, and having the empirical composition " $C_nH_{2m}O_m$ ." Cross and Bevan thought of celluloses from different sources as chemically related but by no means identical substances. Thus a cellulose isolated from spruce wood, which was admittedly different in its *physical* properties from cellulose obtained from the seed hairs of the cotton plant, was also considered *chemically* different from cotton cellulose.

Schwalbe in his "Chemie der Cellulose" evidences this same point of view. He speaks of *celluloses* (*cellulosarten*) and evidently thinks of a number of chemically different celluloses. Schorger<sup>2</sup> in commenting upon the "pentosan content of cellulose" states that differences here point to "distinctly different kinds of cellulose."

This general viewpoint has persisted during the past decade. However, a recent book by Heuser<sup>3</sup> offers a new working hypothesis. Heuser points to recent experiments which have shown that certain cellulose fractions isolated from straw, wood, and cotton are chemically very similar, provided sufficient purification has been used.<sup>4</sup> He therefore suggests that

<sup>1</sup>The early work on isolation of wood cellulose is briefly reviewed in Chapter 3. Analytical data on cellulose are given in another chapter.

<sup>2</sup>*Trans. Wisconsin Acad. Sci. Arts, Letters*, 19, II, 734.

<sup>3</sup>"Textbook of Cellulose Chemistry," translated from the 2nd German edition by West and Esselen, 1924.

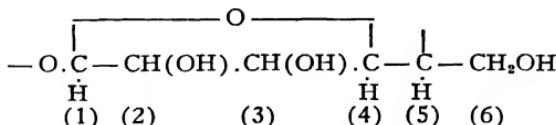
<sup>4</sup>Irvine has also recently shown that one of the polysaccharides of esparto pulp is *chemically* identical with cotton cellulose.

there is only one type of cellulose, and that this is the same chemical individual in all plants. Heuser's hypothesis has been tentatively accepted by a number of investigators. Others have rejected it.

There are, then, two schools of thought with regard to the chemistry of the cellulose of woody tissue. It is because of these divergences of opinion that one investigator may report the presence of 60 per cent of cellulose in a certain wood while another equally capable analyst may report less than 50 per cent of cellulose for the same species. However, these differences in point of view are often not as great as might be expected. They are due in part to differences in interpretation and in the definition of the word "cellulose."

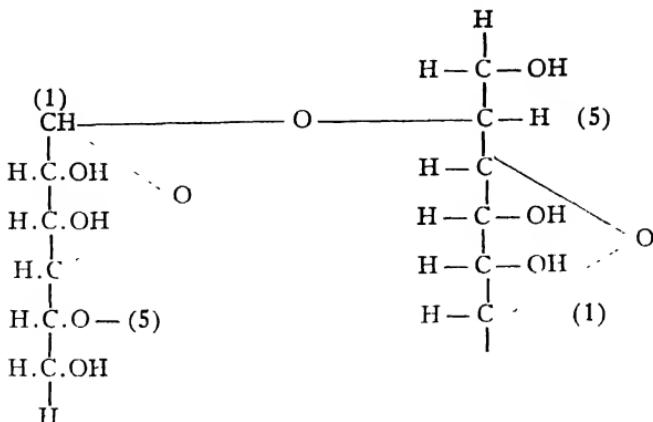
There are a number of polysaccharides intimately associated with each other in the cell wall and some of these polysaccharides show similar physical properties. If we term these collectively "cellulose," then undoubtedly the "celluloses" obtained from different kinds of woody tissue must be considered chemically different. If, however, we recognize that a certain (variable) portion of these polysaccharides in all types of woody tissue is very similar to (if not identical with) cotton cellulose, Heuser's hypothesis of the chemical identity of all celluloses of the higher plants becomes understandable.

Before discussing the nature of wood cellulose further, it may be well to review briefly the properties of cotton cellulose, which in its purified form serves as a standard with which other forms of cellulose have been compared.<sup>5</sup> Cotton cellulose has the composition  $(C_6H_{10}O_5)_n$ , contains three alcoholic hydroxyl groups for every six carbon atoms (as shown by its trimethyl derivative and its triacetate), and on complete hydrolysis yields only *d*-glucose. Acetolysis yields cellobiose octaacetate and glucose pentaacetate. Methylation followed by hydrolysis gives a very high yield of a definite compound, 2, 3, 6-trimethyl glucose. On the basis of these reactions, it has been assumed that the cotton cellulose molecule (or "unit") is made up solely of anhydroglucose residues of the type:



joined through positions (1)' and (5),<sup>6</sup> and that the anhydrocellobiose

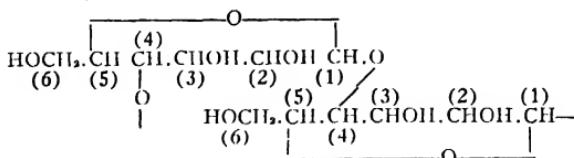
grouping:



must occur in cellulose.<sup>7</sup>

There is at present, however, no definite agreement regarding the limiting yield of cellobiose<sup>6, 8, 9</sup> that may be obtained from cotton cellulose. Investigators are by no means in accord when called upon to decide whether or not the cellulose molecule is made up entirely of cellobiose residues.

Different hypotheses regarding the size of the cellulose molecule have also appeared in the cellulose literature. Views on this subject may be briefly summarized as follows: (a) a relatively enormous molecule made up of a great number of anhydrodextrose residues,<sup>6, 10</sup> many of which go to make up the anhydrocellobiose linkages<sup>11</sup> referred to above; (b) a large glucose apparently has the δ or amylene oxide structure. This requires a fundamental revision of the constitutional formulas suggested for cellulose, which would then contain the (revised) anhydrocellobiose linkage



<sup>7</sup>This is denied by only one recent investigator and his collaborators. Cf. Hess, Weltzien, and Messmer, *Ann.*, 435, 130 (1923), who claim that cellobiose may be a secondary product of acetolysis.

aggregate made up of comparatively small units, each one of which contains the anhydroglucose linkage a relatively small number of times. The units are held together in the larger aggregate by means of secondary valence<sup>12, 18, 7</sup> or in some similar way which is not yet fully determined. From the work of Herzog and his co-workers<sup>14</sup> it appears that the cellulose aggregate is crystalline.

The viewpoint outlined under (a) although still held by individual investigators, has been largely displaced by that referred to under (b). Just what the constitution of the individual cellulose unit really is, still forms the subject of extended debates which are given in another monograph.

Most investigators then, are agreed that the cotton cellulose aggregate is composed of a relatively large number of small units held together by forces which, for the lack of a better name, may be referred to as secondary or auxiliary valences. A crude but rather useful picture of such an

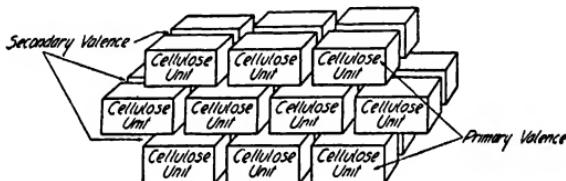


FIG. 3.

hypothesis is given in Fig. 3. The cellulose units may be likened to bricks in a thick wall, the cellulose aggregate. The mortar between these bricks would represent the secondary valence. If the units (bricks) remain undisturbed, but the secondary valence (mortar) is tampered with, changes in state which are so characteristic of cellulose are noted. The individual units or blocks of these units become more or less separated from each other, and a greater surface area is exposed (Fig. 4). Adsorption, which invariably precedes swelling of cellulose, affects the secondary valence. Swelling does not chemically change the little cellulose units; it disturbs the aggregate as a whole.<sup>15</sup> For example, in the swelling caused by the mercerization with alkali, after washing with water, dilute acids (and water), and drying, cellulose shows increased hygroscopicity and an enhanced power of adsorbing substantive dyes, etc. These properties are

<sup>12</sup> Karrer, *Helvetica Chim. Acta*, **4**, 811 (1921); Karrer, *Cellulosechemie*, **2**, 127 (1921).

<sup>13</sup> Esselen, *J. Ind. Eng. Chem.*, **12**, 801 (1920); see also Minor, *Paper*, **25**, 700 (1919).

<sup>14</sup> Hess, etc., *loc. cit.*

<sup>15</sup> *Cellulosechemie*, **2**, 101 (1921), *Naturwissenschaften*, **8**, 673 (1920).

<sup>16</sup> Herzog and Jancke, *Ber.*, **53**, 2162 (1920).

accounted for in our hypothesis by the increased surface area when the units become partially separated from each other. Hydration due to mechanical beating of cellulose with water, and the first stages in the disintegration of cellulose by means of acids may be similarly explained. Complete peptization of cotton in cuprammonium solutions, zinc chloride, and other so-called cellulose solvents, involves a complete disintegration of the cellulose aggregate, with more or less complete separation of the cellulose units from one another. When cellulose is precipitated in "hydrated" gelatinous form from some of its sols, the bricks of the original wall are probably in large measure intact. They approach each other, but they no longer present the same orderly arrangement which was manifested in the original cellulose aggregate (wall). This is indicated by the changes in such substances as viscose.

A different picture obtains when the little units themselves become subject to chemical attack. Such attack often follows the partial or complete

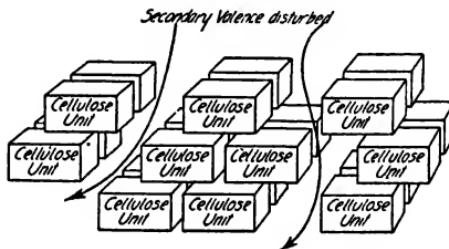


FIG. 4

disintegration of the cellulose aggregate (the wall). It is then that the primary valences within the cellulose units are disturbed. Hydrolysis, acetolysis, and oxidation of cellulose are examples of such attack. Partial hydrolysis—usually referred to under the obscure term "hydrocellulose"—would mean the hydrolysis of a fraction of the number of units originally present in the aggregate. A similar picture would obtain in the case of partially oxidized cellulose (oxycellulose). In either case the partially hydrolyzed or oxidized material may be held in the aggregate consisting in part of unchanged cellulose units.

In practice these two types of changes cannot be readily distinguished from each other. It is almost impossible to drastically alter a cellulose aggregate, by meddling with secondary valence, without causing some chemical change in at least a few of the cellulose units. When the surface area is increased, the chemical resistance of the unit is weakened. This must be borne in mind in seeking to interpret any analytical data in connection with cellulose.

In general, wood cellulose is a residue remaining after more or less drastic treatment of wood to remove lignin and some of the carbohydrates other than cellulose. Such treatment may involve the preparation of chemical pulp by any one of the three well-known processes, or, if the isolation is analytical, may cause the removal of lignin by alternate treatment of the finely divided wood with chlorine and sodium sulfite. In the United States, at least, the term "wood cellulose"<sup>16</sup> has generally referred to the residue isolated by a chlorination method.

The residue when subjected to further purification, such as digestion with cold alkali and careful washing with water and acid, has been termed "alpha" cellulose. The soluble portion removed from  $\alpha$ -cellulose may be separated further into two fractions, the one precipitated by acids and arbitrarily termed  $\beta$ -cellulose; the other remaining dissolved after such treatment and termed  $\gamma$ -cellulose. To the best of our knowledge neither of these fractions from different woods has been critically investigated. Alpha wood-cellulose, as defined, possesses the following properties in common with those of cotton cellulose:

1. It may be hydrolyzed almost quantitatively to *d*-glucose. The rate of hydrolysis after peptization of the cellulose is nearly identical with that of cotton cellulose.<sup>17</sup>

2. On acetolysis it yields cellobiose octaacetate, in amounts very similar to those obtained from cotton.<sup>18</sup>

Wood from Which $\alpha$ -Cellulose Was Isolated	Percentage Yield of Cellobiose Octaacetate Obtained (Based on Theoretical Calculations)
Sugar pine ( <i>Pinus lambertiana</i> ).....	25.8
Longleaf pine ( <i>Pinus palustris</i> ).....	33.0
Red spruce ( <i>Picea rubens</i> ) .....	27.4
Spruce (Sulphite pulp) .....	30.3
Red cedar ( <i>Juniperus virginiana</i> ) .....	26.9
Beech ( <i>Fagus americana</i> ) .....	32.9
Hemlock ( <i>Tsuga canadensis</i> ).....	24.7
Sugar maple ( <i>Acer saccharum</i> ).....	29.2
White oak ( <i>Quercus alba</i> ) .....	25.7
Cotton .....	35.4

3. It shows a crystalline structure practically identical with that of cotton cellulose.<sup>16</sup>

4. On nitration for industrial purposes, it yields nitrates very similar to those of cotton cellulose.<sup>19</sup> Acetylation of cotton or wood cellulose yields very similar cellulose acetates, in nearly identical amounts.<sup>17</sup>

<sup>16</sup> Schorger, *J. Ind. Eng. Chem.*, **9**, 563 (1917); Dore, *ibid.*, **12**, 266 (1920).

<sup>17</sup> Heuser and Boedeker, *Z. angew. Chem.*, **34**, 461 (1921); Heuser and Aiyar, *ibid.*, **37**, 27 (1924).

<sup>18</sup> Wise and Russell, *Ind. Eng. Chem.*, **15**, 815 (1923).

<sup>19</sup> *Loc. cit.*

<sup>20</sup> Schwalbe, *Z. angew. Chem.*, **27**, 662 (1914).

5. When equal amounts of purified cotton cellulose and wood cellulose are dissolved, each in a definite volume of cuprammonium solution under carefully standardized conditions, the specific rotations of these two solutions are practically identical.<sup>20</sup> Thus a cuprammonium solution of cotton representing four molecules of cellulose to ten molecules of copper per 100 liters of solution, showed  $\alpha = -3.36^\circ$ . Under similar conditions a solution of wood cellulose showed  $\alpha = -3.29^\circ$ .

These facts taken by themselves might argue for the identity of cotton and wood cellulose, were it not for the following disconcerting data. Alpha cellulose from coniferous woods has been shown by Sherrard and Blanco<sup>21</sup> to yield small but appreciable quantities of mannose on hydrolysis. Wood cellulose isolated from the *angiosperms* when carefully purified still contains small amounts of furfural-yielding substances, or substances related to furfural,<sup>18</sup> and to a lesser degree this is also true of cellulose separated from conifers.

Another argument against the identity of wood and cotton cellulose has been advanced on the basis of the absence of so-called  $\gamma$ -cellulose from purified cotton, and its presence in appreciable quantities in the cellulose obtained from wood.<sup>22</sup>

In the opinion of the writers, however, analytical data regarding  $\gamma$ -cellulose have no vital bearing on the true nature of wood cellulose. The term " $\gamma$ -cellulose" refers to a fraction, of very uncertain identity, obtained in a convenient but arbitrary analytical procedure, which has never been correlated with problems on the constitution of cellulose. It has been shown that conditions of chlorination influence the amount of cellulose very considerably in the same sample of cotton or wood cellulose. Successive chlorinations, while they do not appreciably affect the total cellulose content, serve to decrease the percentage of  $\alpha$ -cellulose.<sup>23</sup> (Table I.)

TABLE I  
EFFECT OF REPEATED CHLORINATION ON CELLULOSE CONTENT OF COTTON AND SPRUCE

Per Cent	Cotton	Spruce Pulp
"Total cellulose" after single chlorination . . . . .	98.1	96.2
"Total cellulose" after four chlorinations . . . . .	96.9	94.7
"Alpha cellulose" after treatment of original sample with NaOH (17.5 per cent) .. . . . .	97.2	80.8
"Alpha cellulose" after one chlorination . . . . .	91.8	76.7
"Alpha cellulose" after four chlorinations . . . . .	83.5	68.7

This would mean an increase in the  $\beta$  or  $\gamma$ -cellulose content or in both. It would appear, therefore, that  $\beta$  and  $\gamma$ -cellulose may actually be consid-

<sup>20</sup> Hess, *Z. angew. Chem.*, **37**, 996 (1924).

<sup>21</sup> Sherrard and Blanco, *J. Am. Chem. Soc.*, **45**, 1610 (1923).

<sup>22</sup> Wise and Russell, *loc. cit.*; also Schorger, *loc. cit.*

<sup>23</sup> Mahood and Cable, *J. Ind. Eng. Chem.*, **14**, 727 (1922).

<sup>24</sup> Wise and Russell, *J. Ind. Eng. Chem.*, **14**, 285 (1922).

ered, in part at least, derivatives of the original cellulose. They may be produced during the chlorination, and are not necessarily part of the original cellulose aggregate. Needless to say, the formation of alkali-soluble cellulose ( $\beta$  and  $\gamma$ -cellulose) would depend in no small measure on the physical condition (state of aggregation) of the original cellulose. In the case of celluloses which have undergone drastic treatment prior to the cellulose analysis, whether this treatment is due to the action of molds or to a chemical process, lessened resistance to oxidation might be expected, and consequently less  $\alpha$ -cellulose and correspondingly more  $\beta$  and  $\gamma$ -cellulose in the residue after chlorination. *In other words, there is at present no evidence that  $\beta$  or  $\gamma$ -cellulose are necessarily components of the original material from which cellulose has been isolated.*

The question now arises—can these other data be brought into harmony in the formulation of an hypothesis regarding the constitution of wood cellulose? It must be assumed at the outset that the wood-cellulose aggregate is a very variable one. It is doubtful whether the same investigator can succeed in isolating the identical aggregate from the same sample of wood in two successive experiments. This does not mean that the great majority of units in such an aggregate (in the case of alpha wood cellulose) may not be identical with the units in cotton cellulose.

If this is true, the minority units—i.e. those chemically *not* identical with the cotton-cellulose unit—which perhaps make up a part of the wood-cellulose aggregate, might reasonably be considered the units of those carbohydrates which become intimately associated with the cellulose units during the growth of the cell. The fact that some of these adsorbed carbohydrates remain closely associated with the cellulose, even after drastic treatment, when (so-called typical) pentosans, mannans, etc., are dissolved or destroyed by such treatment, is not out of harmony with our general knowledge regarding changes in the properties of substances following adsorption. Purification of wood cellulose always involves the attempted removal of extraneous material with the minimum change in the cellulose. On the other hand, it does not permit the true solution and reprecipitation of cellulose under conditions which might facilitate the removal of extraneous material, and it is common knowledge that solids held by gelatinous precipitates may be exceedingly difficult to remove and that in the past, solid solutions have often been mistaken for chemical compounds. Taking these facts into consideration, and realizing that cotton and wood cellulose have many chemical properties in common, it appears reasonable to formulate an hypothesis for the structure of wood cellulose which is very similar to that advanced for cotton cellulose. In the case of the wood-cellulose aggregate (the wall), most of the units (bricks) appear to be identical with those in the cotton-cellulose aggregate. Varying amounts, and varying types of other units, however, may also be present in the

wood-cellulose *aggregate*, such units becoming associated with the cellulose units during growth. Fig. 5 gives a diagrammatic picture of wood cellulose. Again we have the typical cellulose bricks in the cellulose wall held together by secondary valence mortar, but besides we have a smaller number of other units—mannans, pentosans, or any other type of polysaccharide than can conceivably be formed during the growth of the wall. The number and type of these foreign units depend on the conditions of cell growth, and also on the purification to which the wood cellulose has been subjected. The hypothesis naturally accounts for any mannose that may be found in the hydrolysis mixtures obtained from the cellulose of coniferous woods. It also explains the presence of furfural-yielding substances in the  $\alpha$ -cellulose isolated from wood.

From such an hypothesis we would expect the purified wood-cellulose aggregate to manifest a behavior similar to that of cotton cellulose in cases where the secondary valences are disturbed. Furthermore, we would

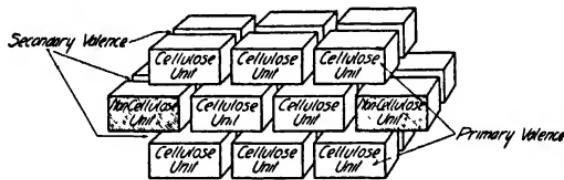


FIG. 5.

expect reactions akin to those of cotton cellulose when wood cellulose is subjected to hydrolysis, oxidation, esterification, and acetolysis. As a matter of fact, the properties of wood cellulose closely approximate those of cotton cellulose, and appear to be in harmony with the hypothesis.

Whereas the foregoing should be taken only as a working hypothesis (and the brick-wall analogy should not be taken too literally), it appears more readily acceptable than one which admits the possibility of a different cellulose unit for each species of wood. Furthermore, it agrees with the more modern viewpoint on cotton cellulose. Its flexibility is apparent, since it accounts satisfactorily for any percentage of pentosans or hexosans that may be found in the cellulose aggregate. On the other hand, like any working hypothesis, it is not necessarily *true*. Up to the present no experimental data appear that might not be accounted for by such an hypothesis. However, wood cellulose has not been explored with the same degree of thoroughness that has marked the study of cotton cellulose. Until this has been done, the preceding hypothesis remains little more than a stimulus to further research.

At present, it appears that methods which can best be applied to the

study of the constitution of wood cellulose are those which have been found serviceable in the studies of other polysaccharides. These would include the technic devised by Irvine and his collaborators in their classical studies at St. Andrews, the physical (X-ray) methods used by Herzog and his co-workers at Berlin, and the physico-chemical studies recently exploited by Hess and his colleagues at the Kaiser-Wilhelm-Institut in Germany.<sup>24</sup>

<sup>24</sup> Cf. *Ann.*, 435, 1 (1923).

## Chapter 2

### Polysaccharides of Wood

Whether or not the preceding working hypothesis on the nature of wood cellulose is accepted, we have ample experimental evidence that the carbohydrates of woody tissue on hydrolysis yield sugars other than glucose. Some of these carbohydrates must be considered as components of an integral portion of the cell wall itself, while others are extraneous (or extraparietal) components, such as some of the gums and the starches. However, it is often a difficult matter to decide whether a polysaccharide giving rise to a particular simple sugar is intra- or extraparietal, and for the present, at least, it appears best to discuss the various polysaccharides of wood together in one chapter.

#### Furfural-Yielding Components of Wood

All woods, when heated with acids under proper conditions, give rise to appreciable amounts of furfural. The immediate precursors of this substance are usually the pentoses: xylose and arabinose, but as these sugars are not present *as such* in wood, it is evident that they result from the hydrolysis of pre-existing polysaccharides. These are usually spoken of as the pentosans. A pentosan which yields xylose on careful hydrolysis was first extracted from various woods by means of alkali by Poumarede and Figuier<sup>1</sup> and later by Thomsen.<sup>2</sup> This was generally termed "wood gum." Tollen and Wheeler<sup>3</sup> hydrolyzed the wood gum isolated from pine and from beech woods, and showed that a product of hydrolysis was a pentose which they termed xylose or "wood sugar." Evidently wood gum was largely composed of xylan. Since then, numerous other investigators have extended and added to Tollen's work.<sup>4</sup> Wood gums are not always composed entirely or even in part of xylans. Thus Johnson and Osborn<sup>5</sup> prepared a gum from birch wood (*Betula alba*) whose composition approximated (none too closely) the formula C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>. On

<sup>1</sup>J. prakt. Chem. (1), 42, 25 (1847).

<sup>2</sup>J. prakt. Chem. (2), 19, 146 (1879).

<sup>3</sup>Ann., 254, 316 (1889); Ber., 22, 1046 (1889).

<sup>4</sup>Cf. Winterstein, Z. physiol. Chem., 17, 381 (1893); Bader, Chem. Ztg., 19, 55 (1895); O'Dwyer, Biochem. J., 17, 501 (1923).

<sup>5</sup>J. Am. Chem. Soc., 18, 219 (1896).

hydrolysis, the material yielded a syrup from which a small crop of crystals—but no xylose—was isolated. To the best of our knowledge the crystalline substance was never identified.

The presence of arabinose-yielding components in wood is indicated by a few scattered references in the chemical literature. Klason,<sup>6</sup> in analyzing the sugars found in sulfite liquor, reports small amounts of arabinose which could be traced back to the carbohydrates of the original wood. O'Dwyer<sup>4</sup> states that the hydrolysis products of oakwood include small amounts of arabinose. Sherrard and Blanco<sup>7</sup> also report the presence of arabinose among the products obtained on acid hydrolysis of white spruce wood. Their test for the sugar depends on the selective fermentation of pentoses by lactic acid bacteria from corn silage ("organism 102"). Fred, Peterson, and Anderson<sup>8</sup> had shown previously that this organism does not ferment xylose. Since Sherrard and Blanco had definitely proved the presence of xylose among the hydrolysis products, and since "organism 102" destroyed an appreciable part of the pentoses, the presence of arabinose was indicated. On the other hand, the presence of arabinose was not proved by definite chemical tests, such as those used in the identification of xylose. A thorough chemical investigation of a number of different woods, with a view towards definitely establishing the presence or absence of arabinose-yielding polysaccharides would appear to be justified.

The total percentage of pentosans in wood--based on the furfural determination—varies considerably with different species of wood. In general, however, the angiosperms give much higher yields of furfural than do the gymnosperms. Thus the pentosan content based on the dry weight of a hardwood, like yellow birch (*Betula lutea*), may be as high as 26 per cent, while the pentosan content of a coniferous wood, such as western yellow pine (*Pinus ponderosa*), may be as low as 5.5 per cent. These differences will be discussed in a subsequent chapter.

Whether or not the greater part of the pentosan of wood is originally in the form of a "gum," or whether it is a component of the cell wall proper has been the subject of some debate. There is every reason to believe that in most woods an appreciable part of the pentosans (certainly of the xylose-yielding components) forms an integral part of the cell wall. This is evidenced by the fact that the so-called "wood cellulose" (isolated by the chlorination method, or by the bisulfite digestion) always retains appreciable amounts of furfural-yielding material. For example, Dore,<sup>9</sup> even after extracting the wood of *Quercus agrifolia* with alkali, found

<sup>6</sup> *Svensk Pappers-Tid.*, **20**, 176 (1917).

<sup>7</sup> *Ind. Eng. Chem.*, **15**, 611 (1923).

<sup>8</sup> *J. Biol. Chem.*, **48**, 385 (1921).

<sup>9</sup> *J. Ind. Eng. Chem.*, **12**, 984 (1920).

nearly half of the original pentosan in the "cellulose" fraction. The presence of large amounts of furfural-yielding substances in the cellulose obtained on chlorination of wood has been clearly demonstrated by other investigators.<sup>10</sup>

A more direct proof of the presence of xylans in the cell walls of spruce wood was obtained by Hägglund and Klingstedt.<sup>11</sup> They isolated a xylan on extraction of spruce sulfite pulp with alkali, hydrolyzed it and definitely proved the presence of xylose among the products of hydrolysis. On the other hand, tests for arabinose in this same pulp gave negative results.

It should be clearly understood that the generation of furfural by the action of hydrochloric acid on wood, or on various components of wood, cannot be taken as a positive index for the presence of pentosans. Schorger and Smith<sup>12</sup> found that a galactan obtained from western larch yielded appreciable amounts of furfural although pentosans were absent from the original material. Similarly, Tottingham and Gerhardt<sup>13</sup> showed that certain fermentable carbohydrates of applewood, which were quite evidently not pentosans, formed the precursors of a part of the furfural obtained on treatment with hydrochloric acid.

The results of the pentosan method must also be interpreted cautiously when applied to crude cellulose (i.e., the fraction isolated by the chlorination method and often spoken of as "Cross and Bevan cellulose"). If this fraction has been partially oxidized during the chlorination process, it may give rise, when treated with hydrochloric acid, to small amounts of



glucuronic acid:  $\text{H}-\text{C}(\text{O})-\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})-\text{CO}_2\text{H}$  which in turn will yield xylose and finally furfural.<sup>14</sup>

It is evident, then, that there are other furfural-yielding components in wood besides the pentosans and that the quantitative determination of furfural lends no sound basis for the calculation of the actual "pentosan content" of a wood. The "pentosan content" must, therefore, be taken as a conventionalized analytical term rather than as one which expresses the true amount of pentose-yielding material in wood.

Besides the furfural-yielding components of woody tissue, there appear to be substances capable of yielding small amounts of an aldehyde that

<sup>10</sup> Schorger, *J. Ind. Eng. Chem.*, **9**, 556 (1917); Mahood and Cable, *ibid.*, **14**, 933 (1922); Ritter and Fleck, *ibid.*, **14**, 1050 (1922); **15**, 1056 (1923); **16**, 147 (1924).

<sup>11</sup> *Cellulosechemie*, **5**, 57 (1924).

<sup>12</sup> *J. Ind. Eng. Chem.*, **8**, 494 (1916).

<sup>13</sup> *Ind. Eng. Chem.*, **16**, 140 (1924).

<sup>14</sup> Tollens and Lefevre, *Ber.*, **40**, 4519 (1907); Heuser's "Textbook of Cellulose Chemistry" (1924), p. 99.

has been generally accepted as a methyl furfural.<sup>16</sup> Judging by the published analytical data the assumption might be made that this methyl furfural emanates from the methyl pentosans of wood. Schorger,<sup>18</sup> however, has pointed out that no methyl pentoses have been obtained from wood itself and his statement, made in 1917, holds true (with a few exceptions) in 1925. The evidence in favor of pre-existing methyl pentosans rests rather insecurely on the results of an uncertain analytical procedure for the determination of methyl furfural. In fact we are not certain that the substance which has been assumed to be methyl furfural is actually this compound. Heuser and his colleagues<sup>17</sup> have shown that small amounts of a hydroxymethyl furfural were produced by the acid treatment of a highly purified cellulose. This substance might be mistaken for methyl furfural. We, therefore, have no trustworthy experimental evidence that methyl pentosans must be reckoned among the components of wood. The "methyl furfural" analysis will be discussed in more detail in a subsequent chapter.

### Hexosans of Wood

Besides the glucosans, (the glucose-yielding polysaccharides, the principal representative of which is "cellulose") wood also contains polysaccharides which on hydrolysis yield mannose, galactose and levulose. Of these, the precursors of mannose and levulose appear to form a part of the cell wall, while the galactans, at least in some of the conifers, are largely extraparietal.

The presence of mannose-yielding components in coniferous woods was demonstrated by Bertrand,<sup>18</sup> Kimoto,<sup>19</sup> Wheeler and Tollens,<sup>20</sup> and Storer.<sup>21</sup> Probably the outstanding quantitative study of the mannan content of the wood of gymnosperms was made by Schorger.<sup>22</sup> He examined twenty-two species of American conifers and found appreciable amounts of mannan in all cases. He also examined six hardwoods, none of which yielded mannose. On the other hand, Fromherz reported the presence of mannan in a sample of *Populus tremula* L.<sup>23</sup> König and Becker<sup>24</sup> report the presence of small amounts of mannans in beech and in birch wood. Storer<sup>25</sup> found mannans in sugar maple, but not in the wood of

<sup>15</sup> Michelet and Sebehan, *Chem. Ztg.*, **30**, 356 (1906), Graw, *Monatsh. Chem.*, **25**, 987 (1904); Fromherz, *Z. physiol. Chem.*, **50**, 209 (1906).

<sup>16</sup> *J. Ind. Eng. Chem.*, **9**, 561 (1917).

<sup>17</sup> *Cellulosechemie*, **4**, 15 and 85 (1923).

<sup>18</sup> *Compt. rend.*, **129**, 1025 (1899).

<sup>19</sup> *Bull. Agri Coll. Tokyo*, **5**, 253 (1902).

<sup>20</sup> *Ber.*, **22**, 1046 (1889).

<sup>21</sup> *Bussey Inst. Bull.*, **3**, II, 13-45 (1902); III, 47-68 (1903); IV, 69-73 (1904).

<sup>22</sup> *J. Ind. Eng. Chem.*, **9**, 748 (1917).

<sup>23</sup> *Z. physiol. Chem.*, **50**, 237 (1906).

<sup>24</sup> *Z. angew. Chem.*, **32**, 155 (1919).

<sup>25</sup> *Loc. cit.*

gray birch, poplar, and willow. In view of these discrepancies the work on mannose content of hardwoods should be extended and correlated since the mannan determination might serve as a valuable means of differentiating chemically between the wood of gymnosperms and angiosperms.

Among the recent investigators, who have made quantitative studies of the mannose-yielding carbohydrates in the cell wall are Sherrard and Blanco,<sup>26</sup> who showed the presence of appreciable amounts of mannose among the hydrolysis products of white spruce wood as well as spruce cellulose; Lenze, Pleus, and Müller,<sup>27</sup> who determined the mannans in wood pulp; Heuser and Dammel,<sup>28</sup> who made a critical study of the mannan determination as applied to pulp and who accepted Schorger's technic; and Hägglund and Klingstedt,<sup>29</sup> who also focussed their attention on spruce sulfite pulp.

In general, the method used for the identification (or determination) of mannans, depends on its hydrolysis to mannose, followed by conversion of the latter to the insoluble mannose phenylhydrazone.<sup>30</sup> The use of mannose bromophenylhydrazone has also been suggested by Lenze, Pleus, and Müller.<sup>31</sup>

Sherrard and Blanco<sup>32</sup> were able to obtain a mannose-yielding polysaccharide from the cell wall of white spruce. They ascribe its formation to a gradual hydrolysis. Cross and Bevan cellulose was subjected to a protracted water extraction. The extract yielded a syrup from which alcohol precipitated a crystalline polysaccharide, corresponding to 12 per cent of the crude cellulose. The material is very soluble in water, but insoluble in the ordinary organic solvents, has a slight reducing action on Fehling solution, and on hydrolysis yields relatively large amounts of mannose (corresponding to about 1/3 of its weight). It also gives rise to quantities of furfural which would correspond to a pentose content of 20 per cent. Further than this, the nature of this interesting polysaccharide has not been studied.

The presence of fructose-yielding polysaccharides in wood has been a mooted point. Krause<sup>33</sup> claims to have shown the presence of fructose among the sugars obtained from sulfite waste liquors. Hägglund<sup>34</sup> also showed the presence of fructose in sulfite liquors and among the products of hydrolysis of spruce wood. On the other hand, König and Becker<sup>35</sup>

<sup>26</sup> *Ind. Eng. Chem.*, 15, 611 (1923).

<sup>27</sup> *J. prakt. Chem.*, 101, 213 (1921).

<sup>28</sup> *Cellulosechemie*, 5, 45 (1924).

<sup>29</sup> *Loc. cit.*

<sup>30</sup> Schorger, *loc. cit.*

<sup>31</sup> *Loc. cit.*

<sup>32</sup> *Ind. Eng. Chem.*, 15, 1166 (1923).

<sup>33</sup> *Chem. Ind.*, 29, 217 (1906).

<sup>34</sup> *Biochem. Z.*, 70, 416 (1915).

<sup>35</sup> *Z. angew. Chem.*, 32, 155 (1919).

reported the absence of fructose, among the sugars of hydrolyzed woods (in the case of pine, fir, birch, and beech), although special efforts were made to isolate this sugar or to demonstrate its presence.

A careful examination of sulfite pulp by Hägglund and Klingstedt<sup>46</sup> clearly showed the presence of fructose-yielding polysaccharides. The hydrolyzed pulp gave numerous color reactions characteristic for fructose, and the sugar was identified by means of the methylphenylosazone and was determined by oxidation with iodine by Willstätter and Schudel's method.<sup>47</sup> Approximately 2.5 per cent of levulan was thus shown to be present.

The presence of small amounts of galactose-producing carbohydrates in wood had been indicated for several decades past by the mucic acid test. Galactans are hydrolyzed to galactose, which in turn may be oxidized by  $\text{HNO}_3$  to mucic acid. Tollens,<sup>48</sup> Krause,<sup>49</sup> Hägglund,<sup>40</sup> and Klason<sup>41</sup> thus showed the presence of galactose in sulfite liquor. Hägglund found small amounts of galactose among the hydrolysis products of *Pinus sylvestris*.<sup>42</sup> Sherrard and Blanco<sup>43</sup> obtained galactose on hydrolyzing white spruce. Fromherz obtained small amounts of mucic acid from the wood of *Populus tremula*. The most noteworthy work on galactans in wood must, however, be accredited to Schorger and Smith,<sup>43</sup> who found that a considerable portion (8-17 per cent) of the wood of western larch (*Larix occidentalis* Nuttall) was water soluble, and that this water soluble material consisted largely of a *galactan*, the composition of which closely approximated  $\text{C}_6\text{H}_{10}\text{O}_5$  and which yielded solely galactose on hydrolysis. Schorger and Smith termed this polysaccharide  $\epsilon$ -galactan, since it appeared chemically different in its properties from other galactans that had been isolated up to that time.  $\epsilon$ -Galactan had the rotation  $[\alpha]_D^{20} + 12.11^\circ$  and was not precipitated from its aqueous solutions by lead acetate. It was isolated as a white granular powder which formed a clear solution in cold and hot water; when heated with 12 per cent HCl it yielded over 6 per cent furfural, but no pentose could be found among its hydrolysis products. Evidently there was no pentosan residue present. This galactan is probably one of the best sources of galactose. Schorger and Smith further showed (by the mucic acid test) that galactans were present in the wood of a number of American conifers. Dore<sup>44</sup> also found galactans in sev-

<sup>46</sup> *Loc. cit.*

<sup>47</sup> *Ber.*, 51, 780 (1918).

<sup>48</sup> Tollens, *Ber.*, 23, 2990 (1890).

<sup>49</sup> Krause, *Chem. Ind.*, 29, 217 (1906).

<sup>40</sup> Hägglund, *Biochem. Z.*, 70, 416 (1915).

<sup>41</sup> Klason, *Svensk. Pappers-Tid.*, 20, 176 (1917).

<sup>42</sup> Cf. Klason, *Arkiv. Kemi. Min. Geol.*, 3, 1 (6) (1908).

<sup>43</sup> *J. Ind. Eng. Chem.*, 8, 494 (1916).

<sup>44</sup> *J. Ind. Eng. Chem.*, 12, 476 (1920).

eral conifers and in oak (*Quercus agrifolia*). König and Becker<sup>45</sup> showed the presence of galactans in birch wood as well as in pine and fir. On the other hand, galactans seem to be largely absent from spruce pulp.

Besides the hexoses referred to, glucose is also a regular component of the products of mild or partial hydrolysis of wood. Thus Klason has reported appreciable amounts of *d*-glucose in the liquor obtained in cooking wood by the sulfite (Ritter-Kellner) process.<sup>46</sup> Hagglund<sup>47</sup> obtained small amounts of glucose by the hydrolysis of pine with 0.5 per cent  $H_2SO_4$  for short time intervals at 155° and at 170° C. Sherrard and Blanco<sup>48</sup> in their comprehensive study of the products of wood hydrolysis have also identified glucose. At first blush it would appear that the sole precursor of this glucose must be the cellulose of wood. In fact, Sherrard and Blanco's quantitative data make it apparent that an appreciable part of the glucose does emanate from this source. As shown in the previous chapter, however, much depends on the accepted definition of wood cellulose. Furthermore, other hexosans of wood are not excluded as the forerunners of *d*-glucose. Pringsheim<sup>49</sup> states that the hydrolytic production of glucose from wood need not necessarily be referred back to cellulose. It may be due to starch, or possibly to a hexosan which may itself take part in the synthesis of cellulose. Starch is one of the extraneous polysaccharides of wood (i.e., it is not associated with cellulose or other polysaccharides of the cell wall). The significance of starch as a reserve stuff in woody stems was first pointed out by Hartig,<sup>50</sup> and other chemists and botanists furthered these investigations. Evidently the detection of starch in the medullary rays of wood has depended largely on color reactions, and the use of the polarizing microscope, coupled with analytical determinations and the use of starch-splitting enzymes. Starch may be hydrolyzed away from woody tissue by the use of amylase or takadiastase. To the best of our knowledge it has never been isolated from wood and subjected to a careful chemical study.

The starch content of the medullary rays varies considerably with species of wood, with the condition of the plant, and with the season. This disappearance and translocation of starch forms a remarkable contrast to the permanency of the cellulose of the cell wall.

The starch content of the wood of fruit trees was investigated by Manaresi and Tonegutti,<sup>51</sup> who showed that in individual cases the starch content was appreciable (e.g., over 3 per cent in pear wood). Beckmann<sup>52</sup>

<sup>45</sup> *Loc. cit.*

<sup>46</sup> *Svensk Pappers-Tid.*, **20**, 176 (1920).

<sup>47</sup> *Loc. cit.*

<sup>48</sup> *Loc. cit.*

<sup>49</sup> "Die Polysaccharide," p. 190.

<sup>50</sup> *J. prakt. Chem.*, **5**, 217 (1835).

<sup>51</sup> *Staz. sper. agrar. ital.*, **43**, 705 (1910).

<sup>52</sup> *Zentr. Biochem. u. Biophys.*, **18**, 379 (1915).

determined the percentage of starch in various hardwoods including birch, alder, maple and elm, and noted some wide seasonal variations (e.g., the spring birch wood contained 3.67 per cent starch, while autumn wood retained less than 1 per cent.

### The Biochemical Nature of the Polysaccharides of Wood

A group designation of "hemicelluloses" was made by Schulze and his co-workers—for those polysaccharides which are relatively insoluble in water, but which are soluble in alkalis and acids and readily hydrolyzed by the latter.<sup>53</sup> This was an arbitrary attempt to differentiate between (a) true cellulose, (b) an intermediate group of carbohydrates, and (c) the reserve foodstuffs like starch and some of the gums. The danger of seeking to make a chemical differentiation on the basis of physical differences or of relative rates of hydrolysis is at once apparent. Even purified cellulose which has been subjected to physical treatment (such as prolonged mechanical beating or disintegration) or to chemical "hydration" may show a marked increase in solubility and invariably shows an increase in the rate of hydrolysis due to an increase in exposed surface—even when no demonstrable change in constitution has occurred. In other words, it is conceivable that by using mechanical methods, we could so change cellulose that it would fall under Schulze's classification of the hemicelluloses.

Evidently the hemicelluloses are polysaccharides which bridge the gap between the insoluble cellulose and the clearly recognized reserve carbohydrates like starch. As a class they may function in part as polysaccharides of the cell wall, in part as reserve material. They appear to lack the "resistance" of true cellulose on the one hand and the "lability" of starch on the other. The classification, therefore, becomes physiological rather than chemical.

At best the collective term "hemicellulose" is a very indefinite one and it would appear to us to be practically impossible to know just where cellulose ends and the hemicelluloses begin. The differentiation is a purely arbitrary one. This has proved a difficulty in arriving at a definite understanding of the term cellulose. The advisability of dropping the word "hemicellulose" is strongly urged by Heuser.<sup>54</sup>

If we assume that the polysaccharides of wood are built up largely of anhydropentose and anhydrohexose residues (other anhydrosugar derivatives are not excluded) it is quite possible that some of the so-called "hemicelluloses" may be not only glucosans, mannans, levulans, galactans, xylyans, and arabans, but mixed polysaccharides such as mannogalactans,

<sup>53</sup> Cf. Czapek, "Biochemie d. Pflanzen," I, p. 420.

<sup>54</sup> *J. prakt. Chem.*, 103, 74 (1921).

galactomannans, xylo-mannans, etc.<sup>55</sup> In other words, the polysaccharides may be represented by the general formulas  $(C_5H_8O_4)_n$  and  $(C_9H_{10}O_6)_n$  or in individual cases by formulas intermediate between these two. However, since we have practically no criteria of purity applicable to the polysaccharides, it is practically impossible to decide whether an isolated polysaccharide fraction is a mixture of two or more distinct substances or whether it represents one chemical individual. This is the same difficulty that is encountered in deciding on the homogeneity of wood cellulose.

The quantitative isolation and identification of definite di- or tri-saccharides derived from the polysaccharides of wood would serve to advance our meagre knowledge of the subject.

Another term of rather dubious significance is the word "pectin" as applied to the components of the middle lamellæ of the cells in woody tissue. Up to the present, we have no convincing experimental evidence that there is a substance or group of substances in the cell walls of wood analogous in chemical behavior to that of the gel-forming pectins found in fruits. These pectins are derivatives of *d*-galacturonic acid. They contain methoxyl groups and are also derivatives of the simple sugars. Ehrlich<sup>56</sup> has described them as "calcium magnesium salts of an anhydro-arabinogalactose methoxyl tetragalacturonic acid." No such pectin has been isolated from wood and if it is present at all, the quantities are small.<sup>57</sup> Despite this, attempts to determine the pectin content of various woods were made by Schwalbe and Becker<sup>58</sup> by applying the method of von Fellenberg<sup>59</sup> which consisted in determining the methyl alcohol split off by cold NaOH from wood and by multiplying the result by 10, an arbitrary factor. This was based on the unproved assumption that the methoxyl content of pectin approximates 10 per cent. Since, however, the methoxyl content of isolated pectin is not definitely known and since no wood pectins have been isolated, Schwalbe and Becker's results (which vary between 1 and 2 per cent) have little significance.<sup>60</sup> Furthermore the recent work of Ritter<sup>61</sup> on the distribution of lignin in the cell wall of wood makes it probable that the components of the middle lamella should be classed with the lignin of wood.

Ritter treated wood samples with various reagents that are commonly regarded as solvents for "pectin substances" or calcium pectate. These

<sup>55</sup> Cf. Pringsheim, "Polysaccharide," p. 184; Czapek, "Biochemie d. Pflanzen," Vol. I, pp 420, 647, 654, III, p 789.

<sup>56</sup> Chem. Ztg., 41, 197 (1917).

<sup>57</sup> Dore, Ind. Eng. Chem., 16, 1042 (1924).

<sup>58</sup> Z. angew. Chem., 32, I, 229 (1919).

<sup>59</sup> Biochem. Zeits., 85, 45-117 (1918).

<sup>60</sup> The authors are indebted to Professor W. H. Dore of the University of California for references and discussion on the pectins.

<sup>61</sup> Ind. Eng. Chem., 17, 1194 (1925).

reagents included aqueous solutions of ammonium oxalate, 2.5 per cent  $H_2SO_4$ , and 3 per cent of HCl. In the case of the last-named reagent wood sections were treated alternately with HCl and 3 per cent NaOH at  $52.4^\circ$  for protracted time periods. At the end of this treatment the middle lamella appeared intact (after staining with ruthenium red). Ritter therefore concludes that the claim made by botanists that the middle lamella is composed chiefly of pectin or calcium pectate (similar to the substance in fruits) is founded on insufficient experimental evidence.

## Chapter 3

### Lignin

Certain organic components of the cell wall (often representing 20-30 per cent of the dry weight of the wood) function in increasing the strength of that wall. These have been grouped together under the collective term *lignin*. Although this word, derived from the Latin *lignum* (wood), was in general use among plant physiologists by the middle of the 19th Century,<sup>1</sup> it still defies a sharp, clean-cut definition. Phytochemists and plant physiologists have reached no agreement on what they mean by *lignin*, and all attempts to circumscribe the use of the word have led to difficulties. Some few years ago, it might have been proper to define lignin as the organic, *non-polysaccharidic* portion of the cell wall, but this definition would certainly be challenged by some of our present-day investigators. The same would be true if we attempted to define lignin on the basis of the brilliant color reactions with the polyhydroxybenzenes—which at one time were believed to characterize the substance.

A survey of the literature on lignin makes it evident that the term should never be applied to any definite chemical compound originally present in the cell wall, and that no lignin fraction isolated from wood<sup>2</sup> has been definitely shown to be a homogeneous substance. All attempts to apply the usual criteria of purity to any specific lignin fraction have been futile and in the isolation of lignin from wood, such drastic measures have been necessary that modification of the lignin could not well be avoided. In other words, it is reasonable to assume that the lignin, once isolated, was no longer identical with the lignin of the cell wall. Furthermore the preparation of lignin derivatives and the many attempts to cause the degradation of lignin into its simpler building stones have furnished relatively little information regarding its constitution. The mechanism of only a few of the lignin reactions has been satisfactorily explained, and only a very few groups in any lignin fraction have been

<sup>1</sup> Czapek, "Biochemie der Pflanzen," Vol. I, 682, states that the term *lignin* was used by the botanist de Candolle.

<sup>2</sup> A lignin recently isolated from flax by Powell and Whittaker, *J. Chem. Soc.*, 125, 357 (1924), appears to be homogeneous or a mixture of closely related isomericides. Lignins obtained from straw may also represent fairly homogeneous fractions. (Beckmann and Liesche, *Z. angew. Chem.*, 34, 285 (1921).)

identified. Consequently it is not surprising that much of the voluminous literature on lignin is purely speculative in character, that these speculations are largely unwarranted by the paucity of reliable experimental data, and that *all* of the constitutional formulas that have been proposed for individual lignin fractions or derivatives are little more than ingenious attempts to harmonize a mass of conflicting data, or to bridge a vast number of experimental gaps.

### Historical Résumé

A brief historical résumé of the studies on lignification may serve to show the conflicting concepts that have arisen in the lignin field, and that are reflected in so much of the experimental work of various investigators. Gay-Lussac and Thenard<sup>3</sup> determined carbon and hydrogen in "wood substance" the so-called *ligncux*, and Petersen and Schödler<sup>4</sup> reported the analyses of 24 common European woods which showed remarkable uniformity in composition. Naturally such analyses gave no clue to the true nature of the cell wall, which appears to have been generally considered a more or less homogeneous substance, despite the fact that individual investigators entertained some fantastic notions regarding its chemical composition.<sup>5</sup>

Probably the first investigator to make serious attempts to interpret his analytical data, and to separate woody tissue into its component parts was Payen.<sup>6</sup> He definitely identified that portion of the wood which resisted the attack of nitric acid and caustic soda and potash, as cellulose, and he also showed that the substances that he could remove from wood by chemical means, were much higher in their carbon content than was the unattacked residue. He pointed out that the hydrogen content of wood was higher than that required for a hydrogen-oxygen ratio of 2:1. Payen's attempts to separate the less resistant portions of the wood into definite fractions were not very successful, and the careful analytical data recorded by Payen were presumably the results of analyses of mixtures of degraded lignin, carbohydrates, and other extraneous substances. Despite Payen's failure to identify these non-resistant components, he rendered an immense service to plant physiologists in formulating an hypothesis that stimulated further research on wood. He showed that the basic and resistant part of the wood was cellulose, and he

<sup>3</sup> Brongniart, Pelouze and Dumas, who critically reviewed Payen's work, quote these investigations in *Compt. rend.*, 8, 51 (1839).

<sup>4</sup> *Ann. der Pharmacie*, 17, 139 (1836).

<sup>5</sup> Czapek, "Biochemie der Pflanzen," I, cites Raspail, *J. Sci. d'Observant.*, 2, 415, as believing that the cell walls of the vessels of wood were composed of lime and gums.

<sup>6</sup> *Compt. rend.*, 7, 1052 and 1125 (1838); 8, 169 (1839); 9, 149 (1839).

assumed that this was mechanically encrusted or impregnated with a less resistant, heterogeneous<sup>7</sup> material that could be removed by suitable chemical treatment of the wood. Payen's hypothesis was accepted by various investigators of the middle of the 19th Century, a number of whom confirmed his analytical data and who assigned the term *lignin* to the less resistant substances of wood. One of these investigators, Schulze,<sup>8</sup> removed what he termed *lignin* from wood by protracted, cold maceration with a mixture of potassium chlorate and nitric acid, which left the residue practically unchanged. His analytical data showed that this residue closely approximated the composition  $C_{12}H_{10}O_{10}$  ( $= C_6H_{10}O_8$  using modern atomic weights). Since the average percentage composition of the total wood substances was shown to be 50 per cent C, and 6 per cent H, and the percentage loss due to the removal of *lignin* could be determined, Schulze was able to calculate the mean percentage composition of this *lignin*, which he concluded to be 56 per cent C, 5.8 per cent H, and 38.2 per cent O. From this he computed the lignin formula  $C_{38}H_{24}O_{20}$  (which by the use of present-day atomic weights would become  $C_{19}H_{24}O_{10}$ ). According to Schulze's data, woody tissue lost from 42-54 per cent of its weight on maceration, and it is now evident that the so-called *lignin* content of wood was much too high and included carbohydrates and their degradation products. In fairness to Schulze, it should be recorded that he himself felt the limitations of this indirect method of analysis, and admitted that no reliable analysis of lignin would be possible, until this substance could be isolated from wood unchanged—an ideal as yet unrealized.

Other chemists who in the main confirmed Payen's work were Mulder,<sup>9</sup> Baumhauer,<sup>10</sup> and Fromberg.<sup>11</sup> However, a few of the early investigators took exception to the "incrustation hypothesis," and among these Fremy<sup>12</sup> strongly opposed Payen's views. He contended that the fibrous elements of wood were composed of a specific substance "fibrose," that the pith and pith rays contained a chemical individual "paracellulose," and that the vessels in wood were made up of a homogeneous material which he termed "vasculose." He entirely discredited the idea of incrustation and gave proximate analytical methods for the isolation of the various fractions of wood that he had described. However, Fremy's hypotheses

<sup>7</sup> Payen at one time assumed at least three distinct chemical individuals. These substances were known as *matières encrustantes*, and represented the non-cellulosic part of the cell wall.

<sup>8</sup> Schulze, *Chem. Centralblatt*, 2 [II], 321 (1857).

<sup>9</sup> Mulder, *Ann.*, 60, 334 (1846).

<sup>10</sup> Baumhauer, *J. prakt. Chem.*, 32, 210 (1844); *Berzelius Jahresber.*, 25, 585 (1846).

<sup>11</sup> Fromberg, *Berzelius Jahresber.*, 24, 462 (1845).

<sup>12</sup> Fremy, *Compt. rend.*, 48, 862 (1859); Fremy and Terreil, *ibid.*, 66, 456 (1868); Fremy, *ibid.*, 83, 1136 (1876); Fremy and Urbain, *ibid.*, 94, 108 (1882).

and his analytical procedure were discarded long before the close of the 19th Century.<sup>18</sup>

Through the studies of Erdmann with the stone cells of the pear,<sup>14</sup> and with fir wood (*Pinus Abies*) (probably *Abies pectinata* DC.)<sup>15</sup> a new hypothesis on lignification was formulated. While Payen and his successors had assumed a mechanical combination between cellulose and the encrusting materials, Erdmann (who had been impressed with the difficulty in removing non-cellulosic material from the cellulose, and with the difference in solubility between pure cellulose and "purified" wood) pointed out the possibility of a chemical union between the various components of the cell wall. Purified pine wood after ten successive treatments with dilute nitric acid yielded 43 per cent of cellulose. Alkali treatment of the wood, followed by acidification, gave a mixture of acetic and succinic acids, and pyrocatechol. A control experiment with purified cellulose showed that alkali fusion did not give rise to pyrocatechol. This suggested an aromatic nucleus in the non-cellulosic portion of the cell wall. Erdmann assumed the presence of a compound between cellulose and the precursor of pyrocatechol, and he termed this compound "lignose." Because he had obtained succinic acid among the degradation products of wood, and since succinic acid was apparently formed in the alkaline fusion of simple sugars, Erdmann also assumed the presence of a simple sugar ( $C_6H_{12}O_6$ ) which he believed to be chemically combined with the lignose. The entire complex of the cell wall he christened "glycolignose," and assigned to it the empirical formula  $C_{80}H_{48}O_{21}$ , which agreed well with his analytical data on *Pinus Abies*. A piece of experimental evidence upon which Erdmann placed much weight in the formulation of his compound hypothesis (and which is still used by defenders of this hypothesis) was the high insolubility of the wood substance in Schweitzer's cuprammonium reagent. This strengthened his conviction that "free" cellulose was not present in wood.

The new hypothesis led to a series of experiments and lively speculations regarding the nature of this chemical union in the cell wall—especially the union between cellulose and the non-resistant lignin. Lange,<sup>16</sup> who had experimented with the alkaline decomposition of oak and beech wood, assumed that this treatment caused a saponification which yielded cellulose with its alcoholic groups, and salts of the acid, lignin. In other words, the chemical union between cellulose and lignin was in the form of an ester. Schwalbe in his "Chemie der Cellulose" (p. 452) has since pointed out that there is no need of assuming *preformed* acid groups

<sup>18</sup> Cf. Sachsse, "Chemie in Physiol. der Farbstoffe," etc., Leipzig, 1877, p. 151; and Cross and Bevan, "Cellulose" (1910), p. 173.

<sup>14</sup> Erdmann, *Ann.*, 138, 1 (1866).

<sup>15</sup> Erdmann, *Ann.*, Supplement V, 223 (1867).

<sup>16</sup> Lange, *Z. physiol. Chem.*, 14, 15 and 283 (1889).

in the lignin of the original wood. The carboxyl groups might result from oxidation taking place during the alkaline treatment. Another hypothesis, formulated at about the same time by Hoppe-Seyler,<sup>17</sup> assumed an ether linking between cellulose and the other components of the cell wall and similar concepts were formed by some of the later investigators. Grafe<sup>18</sup> made the same assumption *in part*, as had Hoppe-Seyler. He pictured the wood substance "lignin" as a mixture of compounds, most of them aromatic in nature. He believed these to be partly "free," partly held by the resinous portion of the wood, and partly in ether-like combination with cellulose. This ether, Grafe assumed, could be decomposed by dilute acids or alkalis. The concept was apparently based on the possible interaction of the alcoholic hydroxyls of the cellulose and the phenolic hydroxyls of some components of the lignin. Cross and Bevan were also strong protagonists of a chemical compound theory, which also presumably presupposed an ether linking, although this was never clearly stated. In their well-known monograph (p. 94), the eminent technologists say: "It has been largely the custom to describe the compound celluloses . . . as mixtures of cellulose and non-cellulose, the latter being generally described as 'encrusting matters' or under the more special term *lignin*. . . . This view will be found inconsistent with the results of the systematic study of the . . . lignified celluloses generally. They are found to be very uniform in composition." This idea of chemical combination was so strongly entrenched in the minds of Cross and Bevan, as a direct result of their researches on jute, that they devised the name *lignocellulose*, to indicate a chemical combination between cellulose and "*lignone*," the latter representing the entire non-cellulosic part of the "molecule." Later, however,<sup>19</sup> the veteran investigators seem to have recanted somewhat, since they say—"The lignin complex may or may not be in chemical union with the cellulose complex"; and in this same work<sup>20</sup> Cross and Doree retire still further from their earlier position.

Many investigators have voiced objections to all theories involving chemical combination between cellulose and lignin. König and Rump<sup>21</sup> present microphotographs in evidence that various components of the cell wall may be readily withdrawn without destroying the structure of the cellulosic tissue. They claim that if cellulose and lignin had been in true chemical combination, the removal of one of the components would have resulted in the physical shattering of the cell wall. Sacchse<sup>22</sup>

<sup>17</sup> Hoppe-Seyler, *Z. physiol. Chem.*, 13, 84 (1888).

<sup>18</sup> Grafe, *Monatsh.*, 25, 987 (1904).

<sup>19</sup> "Researches on Cellulose," IV, 170 (1922).

<sup>20</sup> *Ibid.*, p. 152.

<sup>21</sup> "Chemie u. Structur der Pflanzenzellmembran," 85 (1914).

<sup>22</sup> *Loc. cit.*

regarded the cell wall as a solid solution (somewhat analogous to an alloy) and this viewpoint, in modified form, was accepted by König and Rump.

Perhaps the most modern and generally accepted concept of lignification has been formulated by Wislicenus. Realizing that lignin could not be considered a definite compound, and that the analytical data on lignin varied with nearly every investigator, Wislicenus<sup>23</sup> undertook a dynamic study of lignin formation. He determined the content of adsorbable (colloidal) matter in the cambial saps of a number of trees by treating a given volume of sap with some substance like alumina, and determining the amount of adsorption by comparing the residue obtained by evaporating the treated sap to dryness, and subtracting this residue from that obtained by evaporating an equal volume of untreated sap. These data led him to believe that the period of maximum colloid content of the sap coincided with the period of most rapid and intensive growth. As a result he enunciated the sweeping hypothesis that lignin is composed of the sum total of colloidally dissolved hydrosols (of high molecular weight) which are deposited by adsorption from the formative (Bildungs) or cambial sap upon the surface of the cellulose fiber, the synthesis of which precedes lignification. While the assumption is made that adsorption is primarily responsible for lignification, the possibility of chemical interaction between certain components of the heterogeneous lignin and the cellulose gel is not excluded. Wislicenus was careful to make his hypothesis broad enough to include both the older encrustation theory of Payen, and the chemical compound theories of Hoppe-Seyler, Lange and Grafe.

Although the non-committal adsorption hypothesis has received the endorsement of such critical workers as Schwalbe<sup>24</sup> and has more recently been favorably reviewed by Cross and Doree<sup>25</sup> and by Riefenstahl,<sup>26</sup> it is by no means universally accepted as a working hypothesis for lignification. Schorger,<sup>27</sup> in an article on the gelatinization of lignocellulose, says—"His (Wislicenus') experimental work, upon which is based the theory that the cell wall grows by adsorption by a cellulose gel framework of colloids from the sap, is not particularly convincing from a cytological standpoint. After the formation of the cell by division a layer of pectin is formed between it and its sister cell, this layer later becoming the middle lamella. Layers of cellulose are then deposited, followed by lignification during the later stages. The fundamental syntheses take place within the protoplasm, which is in intimate contact with the cell wall, and there is no reason to believe that any substance other than crystal-

<sup>23</sup> *Kolloid Z.*, 27, 209 (1920); *Cellulosechemie*, 6, 45 (1925).

<sup>24</sup> "Chemie der Cellulose," p. 453 (1911).

<sup>25</sup> *Loc. cit.*

<sup>26</sup> *Z. angew. Chem.*, 37, 169 (1924).

<sup>27</sup> *Ind. Eng. Chem.*, 16, 141 (1924).

loids can pass in quantity through the plasma membrane." Plant physiologists have also voiced their objections to the Wislicenus hypothesis, due to difficulties in technic.

The origin of lignin, and the nature of its precursors have also been the subjects of extensive speculations. There have been two viewpoints on the origin of lignin. One assumes that the cellulose of the cell wall is gradually converted into lignin, while the more generally accepted one assumes that substances other than the cellulose are the lignin precursors. Cross and Bevan<sup>28</sup> advance the following theory: "The process of lignification consists in a series of progressive and intrinsic modifications of a cellulose or oxycellulose tissue, the products of modification remaining associated with the residue of the parent substance in a state of combination or of intimate mixture" König and Rump<sup>29</sup> also suggest the conversion of cellulose into lignin. Wislicenus would naturally agree with the other point of view. The origin of lignin has from time to time been linked with the pentoses or pentosans of wood. Rassow and Zschenderlein<sup>30</sup> showed that lignified tissues low in lignin are usually high in pentosans, and *vice versa*. This finding lends indirect support to the hypothesis that pentosans are the precursors of lignin and recent work indicates that both the pentoses and hexoses may play a rôle in the formation of lignin.<sup>31</sup>

Another assumption that has been made frequently is that certain aromatic compounds occurring in the sap are the forerunners of lignin. Divergent as these various hypotheses appear to be, all of them have some experimental data in their favor. The difficulty has been that some investigators have considered lignin a mixture of closely related individuals, if not one chemical individual. We have no experimental evidence that this is true. In fact much of our evidence points to lignin as a heterogeneous mixture. The true origin of lignin and the mechanism of lignification must await new methods for the isolation and study of lignin.

### Lignin Color Reactions<sup>32</sup>

Certain color reactions have always been used in experimenting with wood and at least some of these have been attributed to the presence of lignin. Perhaps the most striking of these are obtained by the action

<sup>28</sup> "Cellulose," p. 180

<sup>29</sup> *Loc. cit.*

<sup>30</sup> *Z. angew. Chem.*, 34, Aufsatzteil 204 (1921).

<sup>31</sup> Schrauth, *Z. angew. Chem.*, 36, 149 (1923); Schmidt, *Ber.*, 56, 23 (1923)

<sup>32</sup> Detailed discussions of these color reactions are given by P. Casparis, *Pharm Monatsheften*, Nos. 9, 10, and 11 (1920), and by Czapek in his "Biochemie der Pflanzen" (1913), Vol. I, p. 688 *et al.* Such discussions are beyond the scope of the present monograph.

on wood of hydrochloric acid and phenols, and of these the "phloroglucinol reagent" which gives a violet-red coloration with woody tissue has been widely used in testing for lignin. Other reagents like the indoles and the aromatic amines have also served to give characteristic colorations with woody tissue.<sup>33</sup> Results of some of these color tests are summarized in Table II which is taken in part from Czapek's "*Biochemie der Pflanzen*."

TABLE II

COLOR REACTIONS GIVEN BY THE INTERACTION OF WOOD AND VARIOUS PHENOLS  
INDOLE DERIVATIVES, AND AROMATIC AMINES<sup>34</sup>

Organic Reagent Used	Coloration	Investigator
Phenol (in sunlight)	Blue-green	Runge
Phloroglucinol	Purplish-red	Wiesner
Resorcinol	Violet	Wiesner
Orcinol	Reddish-violet	Lippmann
Pyrocatechol	Greenish-blue	Wiesner
Pyrogallol	Blue-green	Wiesner and Ihl
Guaiacol	Yellowish-green	Czapek
Cresol	Green	Czapek
Naphthol	Green	Ihl
Thymol	Green	Ihl
Indole	Cherry-red	v. Baejer
Skatole	Cherry-red	Mattiolo
Carbazole	Cherry-red	Mattiolo
Pyrrol	Red	Ihl
Aniline	Yellow	Runge
p-Toluidine	Yellow	Singer
Naphthylamines	Red	Nickel
Diphenylamine	Red	Ellram
p-Nitraniline	Brick-red	Bergé

The cause of the colorations has been attributed to various components of the wood. Since the colorations disappear after the wood has been treated with  $\text{NaHSO}_3$  or with hydroxylamine, the reactions have often been associated with aromatic aldehydes.<sup>35</sup> Czapek was able to remove from wood a very small amount of substance, apparently an aldehyde, which still gave all the color reactions of the original wood.<sup>36</sup> This substance, which was removed by heating wood with  $\text{ZnCl}_2$  and extracting this solution with  $\text{C}_6\text{H}_6$  or ether, he termed *hadromal* but he was never able to isolate it in sufficient amount to permit its complete identification. This hadromal could not have represented more than a small fraction.

<sup>33</sup> The phloroglucinol reaction was probably discovered by Wiesner, *Sitzber. Wien. Akad.*, **77**, I, 60 (1878).

<sup>34</sup> In the case of phenols and pyrrol derivatives, the color reaction is carried out in the presence of  $\text{HCl}$ . The amine reactions normally involve the  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  salts of the amines. The reactions do not occur after methylation or diazotization of the amine. In the presence of  $\text{HCl}$ , p-nitraniline apparently gives an orange-yellow coloration.

<sup>35</sup> Selwanoff, *Botan. Zentr.*, **45**, 279 (1891).

<sup>36</sup> Czapek, *Z. physiol. Chem.*, **27**, 154 (1899).

tion of that part of wood which is ordinarily termed lignin, and Czapek's work clearly showed (what a number of other investigators had suspected) that the brilliant lignin color reactions were really due to a minor constituent of the wood. This was confirmed by Crocker,<sup>37</sup> who showed that both oil of cloves and oil of sassafras gave colorations with phloroglucinol and with aniline. The absorption spectra of these colored substances were identical with those of the corresponding substances obtained by the interaction of the same reagents with wood. In other words, the substance in wood that is responsible for the coloration is also present in small amount in certain essential oils. Crocker's results show that the color tests do not characterize any appreciable part of the lignin. They are apparently indicators of a small amount of an aldehyde (coniferyl aldehyde?) which normally accompanies the lignin fraction.

Another color reaction which has been used in the examination of certain woods is the so-called Maule reaction.<sup>38</sup> Maule found that a brilliant red coloration is frequently obtained when wood is treated successively with neutral  $KMnO_4$ , aqueous HCl, and  $NH_4OH$ . Crocker<sup>39</sup> noted that only the wood of angiosperms gave distinct red colorations under these conditions. The coniferous woods gave only indefinite yellow or pale brown colors. Crocker's work was later confirmed and extended by Sharma,<sup>40</sup> who found that some 27 species of softwoods failed to give the red coloration (Maule test), while some 40 of the hardwoods responded to the test. The test therefore serves to differentiate sharply between gymnosperms and angiosperms. (*Ginkgo biloba* L. deciduous gymnosperm resembled the coniferous gymnosperms.)

The Maule color reaction appears to be due to deposition of  $MnO_2$ , which then reacts with HCl to liberate chlorine, which forms an unidentified compound with hardwoods that turns red with ammonia. Chlorine will replace  $KMnO_4$  and HCl, and alkalies or organic bases can be used to replace  $NH_4OH$ . Possibly  $Na_2SO_3$  is also instrumental in developing the Mäule coloration, when the Cross and Bevan method of isolating cellulose from wood is used.

Cobalt thiocyanate has also been used as a characteristic reagent for lignified plant tissues. It gives a blue coloration which is not necessarily dependent on the lignin alone.<sup>41</sup> It is evident then, that the foregoing color reactions are not attributable to the *main* part of any lignin fraction. Different minor components may be responsible for different tests, but in the main the colorations appear due to *one* specific minor component—probably an aldehyde, the identity of which is unknown. The

<sup>37</sup> *J. Ind. Eng. Chem.*, **13**, 625 (1921).

<sup>38</sup> *Beitr. z. wiss. Bot.*, **4**, 166 (1901)

<sup>39</sup> *Loc. cit.* Cf. also Casparis, *loc. cit.*

<sup>40</sup> *J. For.*, **20**, 476 (1922).

<sup>41</sup> Cf. Casparis, *loc. cit.*

acetic acid on hydrolysis. After making due allowance for the reversion of methoxyl to hydroxyl, and for the complete removal of acetyl groups during the isolation of the lignin, this value (of 32 per cent) still indicated an excess of free hydroxyl groups originally present in the lignin portion of the wood.

The action of 1 per cent sulfuric acid at 110-130° on pine and beech wood has been shown to yield formic as well as acetic acid.<sup>48</sup> Redwood, extracted with benzene and alcohol, when treated with dilute sulfuric acid, gave small yields of formic acid.<sup>49</sup> There is no reason to doubt these experimental data. On the other hand, they do not force us to the conclusion that formyl groups exist preformed in the lignin of wood. Formic acid may be formed by the treatment of carbohydrates with dilute acids<sup>50</sup> and Schorger's statement that the formic acid obtained from wood probably results from the decomposition of carbohydrates, rather than because of the presence of formyl groups in the wood, appears to be justified.<sup>51</sup> Certain it is that there is no clean-cut experimental evidence to show that formyl groups are present in any lignin fraction, while formic acid has been obtained from the cellulose fractions of wood.<sup>52</sup>

The proponents of the theory of lignification, which assumes a chemical combination between lignin and cellulose of the wood, gave rise to belief that the lignin contained carboxyl groups. A valid objection to this assumption has already been given.<sup>53</sup> While we have ample experimental data that indicate that the carboxyl group is present in some lignin derivatives, we have no sound experimental foundation for the belief that this group (or the ester grouping — C — O — ) must be preformed



in the original wood. Holmberg and Wintzell<sup>54</sup> who investigated the liquor obtained by treating wood with alkali (the black liquor obtained in soda pulp production) isolated a lignin which could be further separated into two fractions, one insoluble and the other soluble in alcohol. The isolation could be effected either by treating the black liquor with an acid (such as sulfuric) or by treating the liquor with carbon dioxide. In either case the lignin fractions were the same. Apparently these fractions (for which Holmberg did not claim chemical homogeneity) contained phenolic groups. There is little reason to assume that they contain carboxyl groups as well. Where these lignin derivatives were

<sup>48</sup> Cross and Tollens, *J. Landw.* 185 (1911).

<sup>49</sup> Dore, *J. Ind. Eng. Chem.*, 12, 472 (1920).

<sup>50</sup> Lieben, *Monatsh.*, 19, 349 (1898).

<sup>51</sup> Schorger, *J. Ind. Eng. Chem.*, 9, 561 (1917).

<sup>52</sup> Dore, *loc. cit.*

<sup>53</sup> Schwalbe, *loc. cit.*

<sup>54</sup> Ber., 54, 2417 (1921).

subjected to more drastic treatment with alkali, however, they gave rise to a number of aliphatic acids and to protocatechuic acid, but the formation of these must be ascribed to a deep seated decomposition of the lignin.<sup>55</sup>

Perhaps the best piece of evidence in favor of a free carbonyl group in lignin is the reducing action of various lignin fractions towards Fehling solution.<sup>56, 57</sup> Aromatic hydrazines have not given products that lend themselves readily to identification and while the lignin components of wood or their derivatives appear to yield unstable compounds with sulfuric acid and the bisulfites, this evidence is not conclusive, since phenolic hydroxyl groups are also capable of yielding unstable bisulfite compounds.<sup>58</sup> Altogether, the presence of carbonyl groups in lignin fractions isolated from wood must be regarded with some uncertainty, and in view of this, attempts to discover whether or not these are *aldehydic* carbonyl groups or *ketone* groups are somewhat premature. As previously emphasized, the brilliant color reactions which at one time were taken as indicative of the aldehyde grouping in lignin, have been traced back to such small amounts of extraneous substances (associated with the lignin) that it is evident that they give no index whatever of the constituent groups of any major lignin fraction. Other investigators have made the assumption that the carbonyl groups in lignin are due to its ketonic structure. Thus Cross and Bevan<sup>59</sup> assume a "diketohexene" and a hydropyrone grouping, but here again adequate experimental data are lacking.

Data in favor of an ethylenic linkage —C=C— in lignin may be traced back to the discovery of a glucoside in the cambial sap of the larch by Hartig<sup>60</sup> and the subsequent finding of Kubel<sup>61</sup> that this substance, which he named coniferin, was widely distributed in coniferous woods. The compound was later shown, by Tiemann and Haarmann,<sup>62</sup> to be a *d*-glucoside of 3-methoxy-4-hydroxy-cinnamic alcohol.

The possible relation of the widely distributed coniferin (or some substance related to it) to the formation of lignin, led Klason to the

<sup>55</sup> However, Rinman, *Svensk. Kem. Tids.*, **23**, 163 (1911) (quoted by Holmberg), reported that two different types of components were found in the black liquor: those that were precipitated by CO<sub>2</sub> ("Humusstoffe") and those that could only be freed from their salts by acids ("Humic acids"). The latter, presumably, were assumed to contain carboxyl groups.

<sup>56</sup> Heuser and Skiolebrand, *Z. angew. Chem.*, **32**, 41 (1919).

<sup>57</sup> Haggblund, *Cellulosechemie*, **4**, 74 (1923).

<sup>58</sup> Fuchs, *Ber.*, **54**, 487 (1921).

<sup>59</sup> *J. Soc. Dyers Colorists*, **32**, 135 (1916).

<sup>60</sup> *Jahresber. Forster*, I, 263 (1861).

<sup>61</sup> *J. prakt. Chem.*, **97**, 243 (1866).

<sup>62</sup> *Ber.*, **7**, 608 (1874); **8**, 1127 (1875); **9**, 410 (1876); **11**, 667 (1878).

studied and that the analytical data are incomplete.<sup>66</sup> Klason had no definite assurance that the yellow precipitates obtained from the lignins were homogeneous substances although the analytical data in his recent work are fairly convincing.<sup>67</sup> While the presence of an ethylenic linking in lignin has not yet been proved and although the assumption of an acrolein group ( $\text{RCH} = \text{CH} - \text{CHO}$ ) must still be taken as a working hypothesis, the recent work of Hagglund<sup>68</sup> on unsaturated aldehydes of known constitution tends to confirm a part of Klason's results. It also serves to strengthen Klason's hypothesis that an acrolein linkage exists in  $\alpha$ -lignin.  $\alpha$ -Ligno-sulfonic acid and compounds of the type of  $\beta$ -sulfopropion-aldehyde show an analogous behavior towards aromatic amines. In solutions that are sufficiently acid these compounds form anils of the corresponding free sulfonic acids. In neutral solution they form the normal amine salts of these acids. When an unsaturated aldehyde of the type  $\text{RCH} : \text{CH} \cdot \text{CHO}$  was treated with  $\text{NaHSO}_4$ , an addition product of the type  $\text{RCH}(\text{SO}_3\text{Na})\text{CH}_2\text{CH}(\text{OII})(\text{SO}_3\text{Na})$  was formed. Compounds of this kind reacted with 2 molecules of  $\beta$ -naphthylamine to form naphthylammonium naphthyliminosulfonates of the type  $\text{RCH}(\text{SO}_3\text{NH}_3^+ \text{C}_{10}\text{H}_7) \cdot \text{CII}_2 \cdot \text{CII} : \text{NC}_{10}\text{H}_7$ , which could be hydrolyzed with acid to form the free naphthylimino sulfonic acid of the type:  $\text{RCH}(\text{SO}_3\text{H})\text{CH}_2\text{CH} : \text{NC}_{10}\text{H}_7$ . It will be noted that according to Hagglund the  $-\text{SO}_3\text{H}$  group enters the *beta* position instead of the *alpha* position as suggested by Klason. Hagglund was able to confirm Klason's work on the interaction of  $\alpha$ -lignosulfonic acid and  $\beta$ -naphthylamine but he leaves unsettled the question of the existence of a cyclic naphthyl amine derivative.<sup>69</sup>

In demonstrating some of the striking analogies between the behavior of coniferyl alcohol and lignin of spruce wood, Klason pointed to the fact that both of these substances give similar *aromatic* compounds when fused with alkali. This finding has lent support to the fairly general belief that an aromatic nucleus is preformed in lignin, since it has been shown repeatedly that the fusion with alkali of various lignin fractions

<sup>66</sup> Hintikka, *Cellulosechemie*, 4, 93 (1923), presents some experimental data that indicate that Klason's proposed mechanism of naphthylamine reaction is not correct.

<sup>67</sup> Ber., 55B, 448 (1922).

<sup>68</sup> *Cellulosechemie*, 6, 29 (1925).

<sup>69</sup> Fuchs, Ber., 54, 488 (1921), takes the position that the presence of an acrolein linkage is not proved and suggests that partially unsaturated cyclic ketones would probably yield similar precipitates with beta naphthylamine after a sulfite cook. The tenacious retention of small amounts of  $\text{HCl}$  by lignin isolated from wood with fuming  $\text{HCl}$  is a rather questionable argument in favor of the double bond. The interaction of chlorine with lignin of wood gives no index of the presence of a double bond in the lignin, since the reaction involves largely *substitution* (not addition) and  $\text{HCl}$  is generated. Cf. Cross and Bevan, "Cellulose," 1910, pp. 104-5.

and lignin derivatives gives rise to protocatechuic acid and pyrocatechol,<sup>70</sup> besides the so-called indefinite "lignic" acids and oxalic acid. A thorough investigation of this fusion was made by Heuser and Winsvold<sup>71</sup> and later by Heuser and Hermann.<sup>71a</sup> The former also give an excellent résumé of the literature. Heuser and Hermann showed that when the KOH fusion of a lignin fraction (isolated from spruce by means of hydrochloric acid) was carried out (in nickel dishes) in air, at 240-250°, the products were largely the "lignic acids," and oxalic acid, while the yields of crude protocatechuic acid and pyrocatechol were 16.4 and 3.7 per cent respectively. They also showed that the pyrocatechol was a secondary product formed from the protocatechuic acid, and that when the fusion was carried out in hydrogen (in place of air), the oxalic acid yields dropped considerably (sometimes to the vanishing point). When an iron crucible replaced the nickel crucible in the fusion, and an atmosphere of hydrogen was used, no oxalic acid was obtained but the pyrocatechol yield rose to 21 per cent, and about 10 per cent of the crude protocatechuic acid was formed. If, however, the fusion was carried out in iron, in an atmosphere of hydrogen, and in the presence of ammonium carbonate, 23 per cent of crude protocatechuic acid, and only 7 per cent of pyrocatechol were formed, with no change in the "lignic acid" yield and without production of oxalic acid. They showed definitely that the fusion of cellulose with KOH yielded neither protocatechuic nor pyrocatechol, irrespective of whether they used iron or nickel crucibles or carried out the fusion in air or hydrogen. In nearly all cases they obtained about 90 per cent oxalic acid, besides appreciable amounts of acetic acid and small amounts of formic acid. Evidently the oxalic acid formation from cellulose was not due to oxidation. Later Heuser and Roth<sup>72</sup> showed that xylan on alkaline fusion yielded only traces of aromatic compounds and that these could be attributed to the presence of impurities in the material used.

Evidently the lignin, and not the cellulose or other polysaccharides of the cell wall, must be the precursor of aromatic substances during alkaline fusion. However, since the temperature of these fusions ranges from 240-280° C., and as the action is extremely drastic, it is dangerous to draw conclusions regarding the constitution of the original lignin on the basis of fusion data. Strupp<sup>73</sup> suggests the possibility that lignin may contain hydroaromatic rather than aromatic nuclei. These might

<sup>70</sup> Erdmann, *Ann.*, Supplement V, 223 (1867); Lange, *Z. physiol. Chem.*, **14**, 15 and 217 (1890), Klasen, *Irkr. Kenn. Berger.*, **6**, 8, Honig and Fuchs, *Monatsh. Chem.*, **40**, 341 (1919); **41**, 215 (1920), Holmberg and Wintzell, *Ber.*, **54**, 2417 (1922).

<sup>71</sup> *Cellulosechemie*, **4**, 49 (1923).

<sup>71a</sup> *Cellulosechemie*, **5**, 1 (1924).

<sup>72</sup> *J. prakt. Chem.*, **107**, 1 (1924).

<sup>73</sup> *Cellulosechemie*, **5**, 6 (1924).

be related to the cyclosaccharides (like inositol), from which aromatic derivatives could be readily obtained.

There are other fragmentary pieces of data favoring the presence of an aromatic (or hydroaromatic) skeleton in lignin. Vacuum distillation of lignin fractions gives rise to phenols and hydroaromatic hydrocarbons.<sup>74</sup> Pressure oxidation of lignin yields small but appreciable amounts of polycarboxylic aromatic acids. Oxidation of lignin with hydrogen peroxide yields some of the same oxidation products as those obtained under similar conditions from vanillin. None of these bits of evidence is entirely conclusive, and none of them gives any indication that an aromatic or hydroaromatic nucleus plays more than a subordinate rôle in the lignin complex, since the amounts of compounds isolated were always under 25 per cent.

To summarize our knowledge on the constituent groups of lignin: of all the groups, linkages or nuclei present in lignin, the presence of only two, the methoxyl and the hydroxyl group, has been definitely proved. The acetyl group is presumably present, but it is difficult to prove that it is actually an integral part of what most investigators please to call "lignin." The preponderance of evidence also favors an aromatic or a hydroaromatic nucleus in lignin, and the presence of an acrolein grouping ( $-C(=O)-CH_2-CH(OH)-C(=O)-$ ) but the experimental data are incomplete.

### Lignin Fractions Isolated from Wood

The isolation of a lignin fraction by the removal of the common polysaccharides of the cell wall usually involves the use of acids, and ordinarily sulfuric and hydrochloric acids are used. The concentration of these acids is an important factor. For example, ordinary, concentrated hydrochloric acid reacts sluggishly with finely divided wood, while 40-42 per cent hydrochloric acid (the fuming acid) removes the polysaccharides quantitatively and leaves most of the non-carbohydrate material in the form of a lignin residue<sup>75</sup> which is easily filtered and washed. The isolation of lignin has also been effected by the action of gaseous hydrogen chloride on moist wood<sup>76</sup> and by heating wood with 1 per cent under 6 atmospheres pressure for 6-7 hours.<sup>77</sup> An older method for isolating lignin, that has been applied by a number of investigators, involves the use of sulfuric acid in concentrations varying from 64 to 72 per cent.<sup>78</sup> The lower concentrations are favored since the isolated

<sup>74</sup> Pictet and Gaulis, *Helvetica Chim Acta*, **6**, 627 (1923).

<sup>75</sup> Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

<sup>76</sup> Krull, modified by König and Becker, *Z. angew. Chem.*, **32**, 155 (1919).

<sup>77</sup> König and Rump, *Z. Nahr. Genussm.*, **28**, 177-222 (1914).

<sup>78</sup> Klason, "Ber. u. Hauptversammlung des Vereins der Zellstoff u. Papier Chemiker Ber.," 1908, 52; *Cellulosechemie*, **4**, 82 (1923); König, *Chem. Ztg.*, **36**, 1101 (1912).

TABLE III  
ULTIMATE ANALYSIS OF SPRUCE AND FIR LIGNIN ISOLATED BY MEANS OF ACID

Lignin Isolated by Means of	Investigator	Per Cent C	Per Cent H	Per Cent Methoxy <sup>1</sup>	Per Cent Pento- sans	Other Data	Reference
Fuming HCl (d.12) . . .	Hägglund	65.47	5.47	14.39	3.69	—	<i>Arkiv. Kemi, Mineral. Geol.</i> , 7, Pt 8, 1 (1918)
Fuming HCl . . .	Heuser, Schmitt, and Gunkel	62.4	6.45	14.65	—	0.41% Cl	<i>Cellulosechemie</i> , 2, 82 (1923)
Fuming HCl . . .	Hägglund	64.06	5.39	14.67	3.89	0.11% N	<i>Cellulosechemie</i> , 4, 76 (1923)
Fuming HCl . . .	Fischer and Schrader	64.79	5.68	13.19	—	—	<i>Ges. Abhandl. Kennt. Kohle</i> , 5, 106 (1920)
Fuming HCl .. .	Industrial Preparation	62.70	5.17	13.6	—	—	<i>Ges. Abhandl. Kennt. Kohle</i> , 5, 106 (1920)
64 per cent H <sub>2</sub> SO <sub>4</sub> , 70 per cent H <sub>2</sub> SO <sub>4</sub> ,	.Klason .Klason	63.97 66.67	5.32 5.47	not detd. ..	1.7 —	—	<i>Cellulosechemie</i> , 4, 82 (1923) Through <i>Z. angew. Chem.</i> , 37, 171 (original reference lacking)
70 per cent H <sub>2</sub> SO <sub>4</sub> , . . . .	Kong 1 per cent HCl under pres- sure . . .	64.85	4.86	" "	—	—	<i>Chem. Ztg.</i> , 36, 1101 (1912)
	Kong and Becker *	68.62	4.99	—	—	—	<i>Papierfähr</i> , 17, 982, 1014, 1171 (1919)
Gaseous HCl . . . .	Kong and Becker *	64.76	5.52	—	—	—	<i>Papierfähr</i> , 17, 982, 1014, 1171 (1919)

\* Lignin probably prepared from Fir ("tannenholz").

lignin retains less acid (after washing), and can be filtered and washed more readily than that isolated with acid of higher concentrations. On the other hand, lignin isolated with 64 per cent acid retains small but appreciable amounts of pentosans, while that obtained by the use of 72 per cent sulfuric acid is pentosan-free, or retains but very small amounts.<sup>79</sup>

The greatest advantage of using strong acids in the isolation of a lignin fraction lies in the simplicity of the operation, but this is partially counterbalanced by the decomposition which lignin suffers as a result of the acid treatment. Sulfuric acid seems to be especially drastic in its action.<sup>80</sup> The product isolated from wood by acids no longer contains some of the constituent groups that are usually associated with lignin. The acetyl group appears to be removed in lignin isolated by hydrochloric acid<sup>81</sup> and an appreciable percentage of the "methoxyl" of the wood is also lost.<sup>82</sup>

There is ample evidence that lignin isolated by acids is not a uniform substance. Table III shows that on ultimate analysis lignin preparations obtained by different investigators from the same species of wood, and under similar conditions, show striking differences in percentage composition.<sup>83</sup> Despite this, lignin isolated by means of fuming hydrochloric acid (sometimes referred to as "Willstatter-lignin") has been widely used by Continental investigators as a starting product in their studies on the constitution of lignin.

Another method of isolating lignin from wood has already been alluded to. The treatment of wood with alkaline solutions under pressure, and the subsequent isolation of a lignin fraction by means of carbon dioxide, sulphuric acid, acetic acid or hydrochloric acid, was used by Holmberg and Wintzell<sup>84</sup> in the preparation of a lignin which could be separated into two fractions. One of these, a grayish yellow powder (termed  $\alpha$ -alkali-lignin), insoluble in alcohol, showed a percentage composition of 65.8 per cent C and 5.9 per cent H (corresponding to the empirical formula:  $C_{40}H_{42}O_{15}$ ). The other fraction termed " $\lambda$ -alkali lignin," soluble in alcohol, contained 67.0 per cent C and 6.2 per cent H.

<sup>79</sup> Dore, *J. Ind. Eng. Chem.*, **12**, 472, 984 (1920).

<sup>80</sup> Hägglund, *Arkiv Kemi. Mineral. Geol.*, **7**, Pt. 8, 1-20 (1918).

<sup>81</sup> Pringsheim and Fuchs, *Z. physiol. Chem.*, **105**, 179 (1919); Heuser and Ackermann, *loc. cit.*

<sup>82</sup> Fischer and Schrader, *Ges. Abhandl. Kärrnnt. Kohle*, **5**, 108 (1920), report that 22 per cent of the methoxyl originally present in wood was not recovered in the isolated lignin. Dore, *J. Ind. Eng. Chem.*, **12**, 984 (1920), also shows that approximately this amount of methoxyl is unrecovered in oakwood lignin, isolated by the means of gaseous hydrochloric acid.

<sup>83</sup> This was clearly demonstrated by Heuser, Schmitt, and Gunkel, *Cellulose-chemie*, **2**, 81 (1921), who prepared a spruce lignin fraction in accordance with Hägglund's directions (*loc. cit.*), but obtained a product very different from Hägglund's lignin fraction. Cf. Table I.

<sup>84</sup> Ber., **54**, 2417 (1921).

(and corresponded to the empirical formula  $C_{40}H_{44}O_{12}$ ). Both of these lignin fractions could be methylated with  $(CH_3)_2SO_4$  in the presence of alkali and these methylated products approached a methoxyl content of 24 per cent, indicating that (assuming the correctness of the empirical formulas) 2 methoxyl groups had entered each lignin fraction and that 6 methoxyl groups were now present in each fraction. It should be emphasized that Holmberg made no claim for the homogeneity of either of these fractions. The substances were amorphous and could not be characterized by any physical constants. Table IV gives analyses of some of the lignin fractions isolated by other investigators from the NaOH extracts of wood.

Table IV indicates that while the lignin fractions isolated from black liquor are subject to variations in composition, they fall within the same general limits as those shown in Table III of lignin fractions isolated by the direct acid treatment of wood. The "alkali-lignins" when fused with alkali also yield products similar to those formed on alkaline fusion of lignin isolated by means of acid. Anderzen and Holmberg<sup>85</sup> studied the oxidation of alkali lignin by 30 per cent  $H_2O_2$ . The products of this oxidation were oxalic, acetic, formic, malonic, and succinic acids. Vanillin when similarly treated also yielded formic, acetic, and succinic acids.

A very recent article by Powell and Whittaker deals with a comparison of "alkali" lignin fractions isolated from different woods:<sup>86</sup> poplar, birch, ash, spruce, larch and pine with lignin prepared from flax shoves.<sup>86a</sup> The products were obtained by digesting the chipped wood with 8-12 per cent aqueous NaOH for 6-10 hours at 140-160° C. The black liquor was then treated with hydrochloric acid and the crude lignin, after washing and drying, was dissolved in aqueous acetone and reprecipitated by pouring into hot 20 per cent HCl. Analytical data indicate that all of the lignin fractions examined may be derivatives of the same polyhydroxycompound, differing only in the number of methoxyl groups which they contain. The hypothetical mother substance of these lignins is termed *lignol*, and  $C_{11}H_{40}O_{16}$  is the empirical formula (tentatively) assigned to it. The "extended" formula for *lignol* is given as  $C_{88}H_{50}O_4(CO)_2(ClO)(OH)_9$ . If this formula is correct, the substance lignol contains nine hydroxyl groups. In the lignin fractions actually isolated, varying numbers of these —OH groups are methylated. As indicated in Table V, the ultimate analysis of such lignin fractions does not serve to distinguish between them. On acetylation, however, those hydroxyl groups of lignol, which were originally unmethylated, were acetylated and from an analysis of these products (acetyl lignin) the total

<sup>85</sup> Ber., 56, 2044 (1923).

<sup>86</sup> J. Chem. Soc., 127, 132 (1925).

<sup>86a</sup> J. Chem. Soc., 125, 357 (1924).

TABLE IV  
ANALYSIS OF LIGNIN FRACTIONS ISOLATED FROM ALKALINE EXTRACTS OF WOOD \*

Investigator	Reference	Method Used	Wood Used	Per Cent C	Per Cent H	Per Cent CH <sub>3</sub> O	Remarks
Lange . . . . .	Z. Physiol. Chem., 14, 223 (1890)	Heating in oil bath at 185°C. with 4.5 parts KOH in aqueous solution, followed by acidification	Oak and Beech	61.5	5.5	—	Fraction soluble in alcohol
Street . . . . .	Dissertation (Göttingen), 1894, p 25	Same as that used by Lange	Spruce	59.0	5.3	—	Fraction insoluble in alcohol
Klason . . . . .	Teknisk. Tids. Kemi. Bergsv. 1893, 17	Acid treatment of black liquor	—	62.9	5.1	to 5.4	—
Klason and Segerfelt . . . . .	Arkiv. Kemi. Mineral. Geol., 4, Pt. 6, 1 (1911)	Isolated from black liquor	—	65.0	6.5	—	
Pringsheim and Fuchs . . . . .	Ber. 56B, 2095 (1923)	Isolated from black liquor, purified by CHCl <sub>3</sub> treatment	—	68.0	6.5	—	
Powell and Whittaker . . . . .	J. Chem. Soc., 127, 132 (1925)	Isolated from black liquor of a sulfate cook	—	65.2	5.4	—	
		Heating with 5 per cent NaOH under 2.5 atm pressure followed by acidification	—	63.3	5.24	11.9 to 12.8	
		Heating with 8-12 per cent NaOH at 140-65° followed by acidification	Spruce	62.2	6.34	15.5	
			Spruce	64.0	5.5	—	

\* Most of the data are quoted from Holmberg and Wintzell.

number of methoxyl and hydroxyl groups in the original materials could be gauged. Similarly the lignin fractions could be partially methylated (up to the introduction of seven methyl groups) and then subsequently acetylated (= acetyl methyl lignin). In all cases the sum of the number of methoxyl and acetyl groups totalled nine. The presence of one aldehyde group in the wood lignin was indicated by quantitative reduction with Fehling solution. Besides this there appear to be two other carbonyl groups, since "one molecule" of methylated wood lignin appears to condense with three molecules of phenylhydrazine. These data, together with those obtained on the bromo-, chloro-, and nitro-lignins, are summarized in Table V.

Criticism of Powell and Whittaker's results would be premature. It is evident that while analytical data suggest the possibility of a parent substance like *lignol*, this substance has not yet been isolated and that there is little evidence of the chemical homogeneity of any of the lignin fractions studied to date. One of the interesting features of the investigation, however, is the fact that Powell and Whittaker's ultimate analysis of the different lignin fractions agree remarkably well with those obtained by Doreé and Hall<sup>66b</sup> by the analysis of their lignosulfonic acid fraction obtained from spruce wood (discussed in Chapter 4 of Part II).

Attempts to study the lignin as it exists in the original spruce wood were recently attempted by Klason and Fagerlind.<sup>67</sup> By means of a long succession of alternate digestions with water and alcohol, approximately 12 per cent of the wood could be dissolved out. Besides removing some carbohydrates, this extraction yielded a resinous material, which, after treatment with petroleum ether (to remove oleoresins) could be resolved into two fractions, one soluble in chloroform, and the other soluble in alcohol and acetic acid. The latter, an optically inactive fraction, amounted to only 1 per cent of the original wood, but showed the usual lignin color reactions and had the percentage composition 63.9 per cent C, 5.74 per cent H, which closely approached that of a fraction isolated by Klason from spruce by means of acid (Cf. Table III) and which was in close agreement with Klason's theoretical calculations on the percentage composition of the lignin actually present in wood.<sup>67a</sup> However, attempts to "dissolve" this lignin by means of the usual bisulfite treatment were not very successful and the material remains unidentified.<sup>68</sup>

<sup>66b</sup> *J. Soc. Chem. Ind.*, **43**, 257 T (1924).

<sup>67</sup> Klason and Fagerlind, "Schriften, Ver Zellstoff in Papier-Chemiker," No. 2; *Glaslon, Ber.*, **55B**, 455 (1922).

<sup>67a</sup> *Klason, Ber.*, **53**, 1864 (1920).

<sup>68</sup> Klason reports ("Über Naturprodukte" (1923), p. 20) that a product similar to this lignin fraction (termed "hemilignin") was synthesized by the action of aqueous acetic acid on coniferin. This substance had the composition 63.92 per cent C and 6.0 per cent H, and was also practically incapable of adding bisulfite.

TABLE V  
SUMMARY OF ANALYTICAL DATA OBTAINED BY POWELL AND WHITTAKER ON ALKALI-LIGNINS

Substance Analyzed	Determination	Source of Lignin						
		Pine	Larch	Flax	Spruce	Ash	Birch	Poplar
Lignin	Per cent C	63.9	63.8	63.4	64.0	63.2	63.2	63.3
	Per cent H	5.8	5.2	5.6	5.5	5.6	5.5	5.8
	Per cent CHO	3.1	—	2.9	3.1	—	3.2	—
	Per cent OMe	11.8	9.0	11.5	11.0	13.3	15.2	12.6
	Per cent CO <sub>2</sub> CH <sub>3</sub>	20.5	23.0	18.9	19.4	17.6	14.5	17.5
Acetyl-lignin	No. of OMe groups	4.0	3.1	3.9	3.8	4.5	5.0	4.3
	No. of acetyl groups	5.0	5.8	4.5	4.8	4.3	3.4	4.3
	Total OMe and acetyl groups	9.0	8.9	8.4	8.6	8.8	8.4	8.6
	Per cent OMe	20.3	19.9	20.4	23.1	20.0	22.4	22.7
	Per cent CO <sub>2</sub> CH <sub>3</sub>	11.1	11.8	10.5	8.0	11.3	8.1	7.5
Acetyl methyl-lignin	No. of OMe groups	6.5	6.4	6.5	7.2	6.4	7.0	7.0
	No. of CO <sub>2</sub> CH <sub>3</sub> groups	2.6	2.7	2.4	1.8	2.6	1.8	1.7
	Total groups in acetyl-methyl-lignin	9.1	9.1	8.9	9.0	9.0	8.8	8.7
Dodecabromo-lignin	Per cent C	28.0	28.2	—	—	28.1	—	—
	Per cent H	1.5	1.6	—	—	1.6	—	—
	Per cent Br	55.2	55.0	54.8	55.2	55.1	54.7	54.9
Acetyl dodeca-bromo-lignin	Per cent OMe	1.8	1.6	—	—	2.4	—	2.1
	Per cent CO <sub>2</sub> CH <sub>3</sub>	9.4	9.8	9.0	9.8	—	—	9.2
Dodeca chloro-lignin	Per cent Cl	35.1	35.5	—	—	—	36.0	—
	Per cent OMe	5.2	4.9	—	—	—	5.1	—
	Per cent C	50.4	50.2	—	—	50.6	—	—
Nitro-lignin	Per cent H	3.8	3.8	—	—	3.9	—	—
	Per cent N	4.2	4.1	—	—	4.3	—	4.2
	Per cent OMe	3.0	3.2	2.6	3.1	3.0	3.3	—
	Per cent C	50.1	—	—	—	49.5*	—	—
Hexachloro-lignin	Per cent H	3.0	—	—	—	3.2*	—	—
Methyl-lignin-phenylhydrazone	Per cent OMe	3.45	—	—	—	3.5*	—	—
	Per cent Cl	20.8	—	—	—	20.4*	—	—
	Per cent N	—	—	—	—	7.5*	—	—

\* Samples prepared from a mixture of equal quantities of the wood lignins.

Other means of isolating a lignin fraction which might approximate the lignin originally present in wood have been suggested, but few intensive studies of such fractions have been made. Hochfelder<sup>90</sup> isolated a lignin by digesting dried spruce chips with phenol at 180° for 48 hours, filtering the pulp, and recovering the lignin substance in the filtrate by distilling off the phenol. This lignin could be split into two fractions, one soluble, one insoluble in ether. The insoluble portion apparently contained free hydroxyl but neither carboxyl nor carbonyl groups. Legeler<sup>91</sup> suggests that the so-called lignins studied by Hochfelder are condensation products of the non-cellulosic portions of the wood with phenol, in which some of the sugars have also played a rôle. Other investigators like Jonas<sup>92</sup> and Schrauth and Quasebarth<sup>93</sup> present evidence that phenol actually forms a condensation product with lignin ("phenol-lignin").

### Examination of "Willstätter Lignin"

Of all lignin fractions isolated from wood (other than "lignin derivatives" formed in certain technological processes) that obtained on treatment with fuming hydrochloric acid (*Willstätter lignin* so-called) has received the most intensive study.

Mild methods for the gradual degradation of Willstätter lignin do not seem generally applicable, and the drastic methods that have been employed by various investigators throw comparatively little light on the constitution of this fraction. Nevertheless their results are suggestive. Lignin is apparently very susceptible to oxidation. Treatment with alkaline permanganate, potassium chlorate, or nitric according to Häggglund<sup>93</sup> gives rise to acetic acid without the formation of oxalic acid. However, the nature of the products of lignin oxidation must depend on the technic used, since both Heuser and his co-workers and König<sup>94</sup> report the production of oxalic acid in large amounts. Fuming nitric acid yielded an unidentified nitrocompound, while ozone<sup>95</sup> yielded formic acid and other substances that were lower in carbon content than was the original lignin. It is evident that the usual methods of oxidation furnish nothing of value regarding the constitution of Willstätter lignin.

A new "pressure oxidation" developed by Fischer and Schrader<sup>96</sup> permitted a more productive exploration of the lignin complex. When

<sup>90</sup> "Beiträge zur Kenntnis der Ligninsubstanzen," through *C. A.*, 15, 2470

<sup>91</sup> Legeler, *Cellulosechemie*, 4, 61 (1923)

<sup>92</sup> Through *C. A.*, 15, 3663.

<sup>93</sup> *Ber.*, 57 **B**, 854 (1924).

<sup>94</sup> *Arkiv. Kemi. Mineral. Geol.*, 7, Part 8, 18 (1918).

<sup>95</sup> *Cellulosechemie*, 2, 112 (1921).

<sup>96</sup> König, *loc. cit.*

<sup>97</sup> *Ges. Abhandl. Kennt. Kohle*, 4, 13 (1919); 5, 221 (1920).

lignin was oxidized in the presence of 2.5 N NaOH under pressure during several hours at 200° C., the indefinite "humic acid" was an important reaction product. If, however, the pressure oxidation was carried out at 300° for 4 hours, a number of well characterized oxidation products were formed. These included 8.3 per cent aliphatic acids and 3.1 per cent aromatic acids. The former included formic, oxalic, succinic, and fumaric acids, while the latter were comprised of benzoic, phthalic, mellitic, and benzopentacarboxylic acids.<sup>97</sup> The isolation of these aromatic bodies is of more than passing interest. While they fail to account for the major portion of Willstätter lignin, they strongly suggest the presence—in this fraction—of a central aromatic or hydroaromatic nucleus.<sup>98</sup> However, the possibility of other cyclic nuclei and of aliphatic side chains is certainly not excluded, and it is necessary to interpret pressure oxidation data with due caution. At temperatures ranging from 200-300° and in the presence of alkali, the formation of these acid products may well be due to secondary reactions.

### Reduction of Lignin

Willstätter and Kallb<sup>99</sup> have investigated the hydrogenation of Willstätter lignin (obtained from beech and red spruce) and compared the products with those obtained under similar treatment from other phytochemical products. When the lignin fractions were heated at 250° for 4-5 hours with hydriodic acid and phosphorus, they yielded as the final product (unaltered by further treatment) a mixture of hydrocarbons that could be separated into a liquid (acetone soluble) portion, and a solid (acetone insoluble) portion. Intermediate fractions included heterogeneous ether-insoluble substances and an acid substance. The hydrocarbon fractions were themselves mixtures and formed an *analogous* (*not* an homologous) series of hydrocarbons ranging in molecular weight from 166 to 842. The liquid mixture had an average composition of 87.81 per cent C and 12.04 per cent H, while the solid portion averaged 88.66 per cent C and 11.47 per cent H. The mean empirical formula calculated for the *entire* mixture closely approximated  $C_6H_4$  or  $(CH_1)_n$ , and the properties of the products recalled those of the hydroaromatic hydrocarbons. It became evident that the hydrocarbons were not formed through the intermediate (well-known) transformation of a hexitol into hexyl iodide, since the final hydrocarbon mixture could not be obtained from iodohexane, while it *could* be obtained from mannitol. Similar hydrocarbon mixtures were also obtained when humin-like substances,

<sup>97</sup> Fischer, Schrader, and Frederick, *Ges. Abhandl. Kennt. Kohle*, 6, 1 (1921).

<sup>98</sup> The fact that cellulose, under similar conditions of pressure oxidation, does not yield similar products serves as a means of differentiating between these two components of the cell wall.

<sup>99</sup> *Ber.*, 55, 2637 (1922).

cotton cellulose, xylose, and dextrose were subjected to the same drastic hydrogenation. Here, however, the quantitative results showed marked differences, as indicated in Table VI.

TABLE VI  
COMPARISON OF RESULTS OBTAINED BY WILLSTÄTTER AND KALB ON HYDROGENATING LIGNIN AND VARIOUS CARBOHYDRATES

Starting Product (100 g.)	Ether-Insoluble Fraction in Grams	Total Yield Hydrocarbons	Grams Liquid Hydrocarbons	Grams Solid Hydrocarbons
Spruce lignin . . . . .	23	28	16	10
Beech lignin . . . . .	23	32	15	17
Humin-like substance . . . . .	47	20	10	10
Cotton cellulose . . . . .	9	20	8	12
Glucose . . . . .	3	17	11	4
Xylose . . . . .	14	16	8	7
Mannite . . . . .	3	16	12	3

Willstätter and Kalb explain the formation of the analogous series of hydrocarbons by assuming that a reactive intermediate product is formed during hydrogenation and that this can polymerize through a "carbon condensation." The polymerization apparently stops at various stages (as indicated by the different molecular weights of the final products) due to accompanying progressive hydrogenation. At each stage completely hydrogenated hydrocarbons are formed, and these have lost their power to polymerize further. It is suggested that the intermediate products may be furan derivatives or diolefines.

Since cellulose and the humin substances give higher yields of the hydrocarbons of high molecular weight than does the glucose, Willstätter and Kalb assume that the skeletal nucleus of the reactive intermediate substances may be preformed to a large extent in the parent substances. In other words, it is not necessary to assume extensive *preliminary degradation* during the hydrogenation of either lignin or cellulose, and from this follows the hypothesis that there may be a relationship between lignin and the polysaccharides of the cell wall. This hypothesis is at variance with those of many other investigators but it may perhaps be brought into harmony with the seemingly conflicting data of these other workers. Attempts that have been made to effect this reconciliation will be briefly treated in the next chapter.

The hydrocarbons obtained by Willstätter's hydrogenation of lignin have not been definitely identified. However, Schrauth<sup>100</sup> showed that one of Willstätter and Kalb's hydrocarbon fractions was at least very similar to a product obtained by Schrauth and Göring by the intramolecular removal of water in 1-*o*-bicyclohexyl-2-cyclohexanone, followed by com-

<sup>100</sup> Z. angew. Chem., 36, 149-52 (1923).

plete hydrogenation of the molecule. The properties of Schrauth and Göring's product ( $C_{14}H_{30}$ ), the fully hydrogenated 9, 10-benzophenanthrene, and of Willstätter's fraction ( $b_{4mm}$  150-70°) are given in the following suggestive table (Table VII), which also shows the similarity between another of Willstätter's hydrocarbon fractions and the cyclohexylcyclohexane described by Borsche and Lange.<sup>101</sup> The hydrogenation of Willstätter lignin in a zinc dust distillation has been carried out by Karrer and Bodding-Wiger<sup>102</sup> but the results are inconclusive. Here the reduction finally led to a series of fractions from which a solid hydrocarbon melting at 210-212° C. was isolated. This compound had the approximate empirical formula  $C_6H_6$ . Other compounds were not identified but all fractions had relatively low molecular weights (ranging from 162 to 250) and in this at least they resembled the fractions obtained by Willstätter and Kalb.

### Degradation of Lignin and the Pentosan Question

The action of mild hydrolytic agents on Willstätter lignin has not been extensively investigated. Hagglund<sup>103</sup> in a preliminary communication reported that on heating Willstätter lignin with successive portions of 3 per cent HCl, he obtained appreciable amounts of unfermentable sugars which were shown to consist largely of arabinose. After one hydrolysis, over 15 per cent of sugar was obtained. Succeeding hydrolyses also yielded sugars but evidently the degradation of lignin became more sluggish and sugar yields decreased with each succeeding hydrolytic treatment. Because of the great importance of the subject, Hagglund's work requires amplification and confirmation.

Whether or not pentosans or furfural-yielding bodies are actually part and parcel of Willstätter lignin has formed the subject of several scientific debates<sup>104</sup>. The consensus of opinion seems to be that the presence or absence of pentosans in lignin depends on the technic used in isolation and that Willstätter lignin can be prepared which no longer responds to the furfural test. However, Schmidt, Geissler, and Arndt<sup>105</sup> report that when Willstätter lignin which is apparently pentosan-free, is treated successively with  $ClO_2$  and  $Na_2SO_3$ , a water soluble pentosan is actually isolated which gives the usual pentosan reactions. His explanation of this puzzling phenomenon is that only after the chlorine dioxide and sulfite have caused the removal of the aromatic encrusting bodies of the lignin can the suppressed "encrusting pentosans" be isolated and

<sup>101</sup> *Ber.*, **38**, 2769 (1905).

<sup>102</sup> *Helvetica Chim. Acta*, **6**, 817 (1923).

<sup>103</sup> *Ber.*, **56**, 1866 (1923).

<sup>104</sup> Cf. Hagglund and Malm, *Cellulosecheme*, **4**, 73, 85 (1923); Heuser, *ibid.*, **4**, 77, 85 (1923).

<sup>105</sup> *Ber.*, **56**, 23 (1923).

TABLE VII  
HYDROCARBONS OBTAINED BY HYDROGENATION OF LIGNIN BY WILLSTATTER AND KALB  
COMPARED (BY SCHRAUTH) WITH OTHER POLYCYCLIC HYDROCARBONS

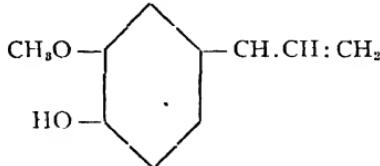
Hydrocarbon Prepared by	Boiling Point	Pressure at B. P.	Per Cent C	Per Cent H	Atomic Ratio C. H. <sub>x</sub>	Molecular Weight	<i>d</i> <sup>20</sup>	Nature of Hydrocarbon
Willstatter and Kalb.....	150-170°	4 mm.	87.85	12.68	C. H. <sub>1.18</sub>	243.8	0.9500	From lignin
Schrauth and Goring.....	175-176°	17 mm.	87.81	12.31	C. H. <sub>1.18</sub>	246.3	0.9425	Hydrogenated 9, 10-benzophenanthrene
Willstatter and Kalb.....	200-230°	Atmospheric	85.95	13.10	C. H. <sub>1.18</sub>	166.7	0.8717	Fraction from hydrogenated lignin
Borsche and Lange .....	234-235°	Atmospheric	86.66	13.34	C. H. <sub>1.18</sub>	166.2	0.8702	Cyclohexyl-
Willstatter and Kalb .....	135-150°	4 mm.	87.77	12.66	C. H. <sub>1.18</sub>	215.1	0.9310	cyclohexane Fraction from hydrogenated lignin
Hypothetical compound ..	—	—	87.16	12.83	C. H. <sub>1.18</sub>	220.2	—	Hypothetical pernyrodimethyl phenanthrene

examined. According to Schmidt, the cell membrane consists principally of two (heterogeneous) substances: (1) the "skeletal substance" (made up of cellulose, "hemicelluloses" and pentosans all unattacked by  $\text{ClO}_2$ ), (2) the encrusting materials (made up of hexosans and pentosans which are coupled with another substance in such a way that their presence cannot be detected until this substance is removed by  $\text{ClO}_2$ ). In other words, the  $\text{ClO}_2$  treatment seems to resolve the non-cellular portion of the wood into an alcohol insoluble pentosan-containing polysaccharide fraction and an alcohol-soluble fraction—the latter representing the material which reacted with  $\text{ClO}_2$ . Although the hypothesis of Schmidt is based on painstaking experimental work and has been hailed by Pringsheim<sup>106</sup> as an important contribution to the chemistry of lignin, it has been refuted by Heuser<sup>107</sup> and Heuser and Merlau.<sup>108</sup> The question of the polysaccharidic nature of the lignin remains an open one—awaiting further experimental results.

### Vacuum Distillation of Lignin

The products of vacuum distillation of lignin are quite different from those obtained when the common disaccharides are submitted to similar treatment. Tropsch,<sup>109</sup> distilling a Willstatter (spruce) lignin under 1-12 mm. pressure at a temperature not exceeding 450°, obtained about 9-11 per cent of a tar, 19-23 per cent of an aqueous (acid) solution, and 53-55 per cent of coke. The greater part of the tar was soluble in either  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  solutions. Less than 2 per cent was removed by  $\text{NaHSO}_3$ , and the residue from these treatments amounted to about 7.5 per cent.

Pictet and Gaulis<sup>110</sup> working independently with a lignin prepared industrially by the action of fuming HCl on spruce wood, carefully examined the components of a tar obtained in a vacuum distillation carried out at 350-390° C. and at 5-25 mm pressure. The greenish-brown fluorescent tar obtained in this way represented only 15 per cent of the total lignin and of this tar about 11 per cent was insoluble in alkali and soluble in ether. The alkali soluble fraction of the tar was treated with acid, but not exhaustively studied. In this fraction, however, eugenol



<sup>106</sup> "Die Polysaccharide," 1923, p 101.

<sup>107</sup> *Ber.*, **56**, 907 (1923).

<sup>108</sup> *Cellulosechemie*, **4**, 101 (1923).

<sup>109</sup> *Brennstoff Chem.*, **3**, 321 (1922).

<sup>110</sup> *Helvetica Chim Acta*, **6**, 627 (1923).

was definitely identified and the investigation is being continued. The smaller, ether soluble fraction was shown to consist of a mixture of saturated and unsaturated hydrocarbons, of which those listed in the following Table VIII were isolated.

Pictet and Gaulis' distillation evidently yields a certain proportion of hydroaromatic hydrocarbons as well as phenols. These findings lend further support to the various bits of evidence that the aromatic nucleus is present in lignin. However, Pictet conservatively points to the fact that only a very small fraction of the lignin complex has actually been explored and that Willstätter lignin is evidently a mixture containing a number of components that differ markedly in chemical properties and that presumably the lignins from different sources are quite different. Pictet's work on vacuum distillation of lignin has an interesting bearing on the controversy raging over the origin of coal.

TABLE VIII  
HYDROCARBONS ISOLATED FROM PRODUCTS OF VACUUM DISTILLATION OF WILLSTÄTTER LIGNIN

	Hydrocarbon	Boiling Pt	$d_4^{20}$	(n) <sub>D</sub>	Other Data
Saturated	$C_{15}H_{30}$	235-40°	0.8091	1.4468	Probably identical with a hydrocarbon found in "vacuum tar" from coal
	$C_{14}H_{30}$	260-70°	0.8138	1.4532	
	$C_{16}H_{30}$	270-80°	0.8218	1.4541	
	$C_{18}H_{34}$	315-20°	0.8579	—	
Unsaturated	$C_{18}H_{30}$ (methylene)	m.p. 62-3°	—	—	Found in vacuum coal tar.
	$C_{11}H_{16}$	200-10°	0.8964	1.5119	Found in vacuum tar.
	$C_{12}H_{16}$	230-40°	0.9172	1.5226	Tetrabromo derivative $C_{18}H_{14}Br_4$ , m. 193°.
	$C_{13}H_{16}$ (?)	250-60°	0.9372	1.5422	

### Distribution of Lignin in Wood

In Chapter 2 we referred briefly to the fact that pectins were presumably absent from the middle lamella of woody tissue. Ritter<sup>111</sup> has made a study of the microscopical changes that occur when lignin is isolated from wood by means of acid or when cellulose is isolated by a chlorination method which removed the lignin. When thin wood sections (basswood, etc.) were chlorinated for 3 minutes on a glass slide, the color of the middle lamella changed to an orange yellow. Upon addition of hot  $Na_2SO_3$ , the middle lamella became wine colored and gradually

<sup>111</sup> Ind. Eng. Chem., 17, 1194 (1925).

dissolved. After 3-4 such chlorinations, each followed by sulfite treatment, the middle lamella had disappeared completely. On the other hand, when wood sections were treated with 72 per cent  $H_2SO_4$ , that part of the cell wall which transmitted polarized light (i.e. the secondary layer) swelled and gradually dissolved, except for a small amount of finely divided residue. *Under these conditions the middle lamella remained intact.* Evidently then the material which the chemist has usually designated as lignin is found largely in the middle lamella. A smaller amount is present in the secondary layer (i.e., what Ritter terms "the cell wall").

Ritter devised a technic by which these two types of lignin could be separated and investigated further. Small cubes of wood 3 mm. on edge (after extraction with alcohol-benzene and boiling  $H_2O$ ) were treated for 24-36 hours with 72 per cent  $H_2SO_4$ . The acid mixture was then diluted with water to 3 per cent and boiled for 5 hours and the finely divided lignin particles separated and filtered on a crucible and washed with water. The bulk of the "lignin" (the substance of the middle lamella) retained a continuous structure and the shape of the original block of wood. This lignin network was washed repeatedly with hot water to remove the amorphous lignin of the secondary layer. While a complete separation of the two lignin types was probably not effected, Ritter was able to obtain roughly quantitative results. The two different kinds of lignin were then separately weighed. In the case of red alder, the middle lamella lignin contained 13.6 per cent methoxyl while that of the remaining cell wall contained only 4.8 per cent MeO. Similarly in western white pine the middle lamella lignin (not quite free from cellulosic material) contained 10.8 per cent methoxyl while the lignin of the secondary layer contained 4.3 per cent MeO. Ritter has thus developed an approximate method for the quantitative separation of at least two lignin types and has opened a new field of investigation. His work is a confirmation of the hypothesis that the "lignin" of wood is non-homogeneous.

## Chapter 4

### Lignin Derivatives and the Constitution of Lignin

#### Halogen Derivatives

The chlorine derivatives of a lignin fraction were probably first studied by Cross and Bevan<sup>1</sup> but their work was carried out largely on jute. According to their statements, the chlorination of jute yielded a definite "lignone chloride" represented by the empirical formula:  $C_{19}H_{14}Cl_4O_9$  ( $= 26.7$  per cent Cl) and "allied to mairogallol and leucogallol" (products of the chlorination of pyrogallol), in combination with a furfural-yielding complex. A bromo derivative of lignin, containing 23.3 per cent Br, was also described by Cross and Bevan.<sup>2</sup>

In an analogous study of the chloro derivatives of spruce lignin made by Heuser and Sieber,<sup>3</sup> a product was obtained containing 47.03 per cent C, 4.59 per cent H and 22.66 per cent Cl but which was not homogeneous and which yielded neither pyrogallol derivatives nor furfural (when distilled with acid). Other halogen derivatives of lignin have been prepared. Holmberg<sup>4</sup> obtained a lignin chloride by chlorination of Willstätter lignin, which contained about 41 per cent Cl, and a bromide which contained 64-65 per cent Br. Neither of these were homogeneous substances. On the other hand, Jonas who also chlorinated Willstätter lignin<sup>5</sup> claims to have carried out reproducible experiments and to have obtained the identical lignin chloride whenever he chlorinated under careful cooling. It is evident that a future critical study of the halogenation reactions will be necessary before any statement can be made regarding the homogeneity of any halogen derivatives of wood lignin. The important rôle played by chlorination in the analysis of wood and in the Cataldi-Pomilio and de Vains processes for delignifying wood would certainly warrant such a study. The introduction of halogen atoms into lignin fractions has been variously taken as evidence of the ethylene linkage and of the presence of an aromatic (or hydroaromatic) nucleus in

<sup>1</sup> *J. Chem. Soc.*, **38**, 666 (1880), *et al*

<sup>2</sup> *J. Chem. Soc.*, **41**, 96 (1882).

<sup>3</sup> *Z. angew. Chem. (Aufsatz)*, **26**, 801 (1913)

<sup>4</sup> *Arkiv. Kemi Mineral. Geol.*, **7**, Pt. 8, 1 (1918).

<sup>5</sup> *Z. angew. Chem. (Aufsatz)*, **34**, 289 (1921).

lignin. But, on the basis of conflicting or incomplete experimental data, such interpretations appear premature.

### Alkylated Lignin

The presence of hydroxyl groups in isolated lignin fractions is clearly indicated by alkylation experiments. Heuser, Schmitt and Gunkel<sup>6</sup> were able to increase the methoxyl content of a Willstätter lignin from 14.7 to 26.3 per cent, by successive methylations, using 10 per cent NaOH and an excess of dimethylsulfate. This "methyl lignin" could be gradually demethylated by heating in a sealed tube with 5 per cent HCl at 170-180° C. The rate of demethylation was slow and the completely demethylated product (obtained after four successive treatments with HCl) was quite different from the original lignin. Degradation of the lignin was indicated where attempts were made to remethylate the methoxyl-free product. Remethylation never yielded products containing more than 6 per cent methoxyl.

One of the interesting features of this investigation lies in its demonstration of the difficulty in obtaining reproducible results in synthesizing lignin derivatives. Previously, Heuser and Lindborn<sup>7</sup> carried out the methylation of a Willstätter lignin fraction which resulted in a methyl-lignin containing 34.6 per cent methoxyl. This high methoxyl content may have been due to polysaccharides retained in Lindborn's lignin fraction, since the presence of these carbohydrates would account for an increase in the percentage of hydroxyl and subsequent methylation would cause a marked increase in the methoxyl content.

Reference has already been made to the "methyl lignins" prepared from  $\alpha$ - and  $\lambda$ -lignin fractions isolated from black liquors by Holmberg and Wintzell.<sup>8</sup> These investigators also used alkali and dimethylsulfate, but in neither case did they repeat the methylation until the methoxyl content of their lignins remained constant. Both of the "alkali lignins" studied, yielded methyl lignins containing approximately 23 per cent of methoxyl.

### Acylated Lignin

The acetylation of lignin has already been briefly mentioned. Heuser and Ackermann<sup>9</sup> acetylated a Willstätter spruce lignin fraction (containing 13 per cent methoxyl and no pentosans) by five different methods, giving special consideration to the conditions for maximum acetylation without hydrolysis of pre-existing groups. When lignin was heated

<sup>6</sup> *Cellulosechemie*, 2, 81 (1921).

<sup>7</sup> Cited in *Cellulosechemie*, 2, 81 (1921). (Original reference not given.)

<sup>8</sup> *Loc. cit.* (Cf. previous chapter.)

<sup>9</sup> *Loc. cit.* (Cf. previous chapter.)

with a mixture of acetic anhydride and pyridine for 1.5 hours on a water bath, maximum acetylation was obtained, and the *lignin acetate* thus formed yielded 32 per cent acetic acid on hydrolysis ( $\approx 23.3$  per cent  $\text{CH}_3-\text{C}-$ ). Continued heating for 1.5 hours caused a marked



decrease in the acetyl value, the product giving only 16.9 per cent acetic acid on hydrolysis. A similar maximum in acetylation was reached ( $\approx 32.4$  per cent acetic acid) when the original lignin was heated at the boiling point with acetyl chloride for two hours. Continued heating also caused partial hydrolysis. On heating the lignin with a mixture of acetic anhydride, acetic acid, and a few drops of fuming nitric acid for 1 hour, a product yielding 31 per cent acetic acid was formed. Continued heating for another hour gave a product yielding only 15 per cent acetic acid, but further heating for 3-8 hours longer caused *reacetylation* and gave rise to a product yielding nearly 43 per cent of acetic acid (and 6.4 per cent methoxyl) on hydrolysis. This high acetyl value is apparently due to a fission of part of the original methoxyl, followed by an acetylation of the regenerated hydroxyl groups. Acetic anhydride alone, or acetic anhydride and sodium acetate, proved to be rather sluggish acetylating agents.

### Lignin Derivatives of Waste Sulfite Liquor—The Ligno- or Lignin-sulfonic Acids

Of all the lignin derivatives subjected to close study, those produced by the action of sulfite liquor ( $\text{Ca}(\text{HSO}_3)_2$  and  $\text{H}_2\text{SO}_3$ ) on coniferous woods hold front rank. Since this liquor represents the waste of the sulfite pulp industry and since it holds in solution much of the non-cellulosic material of the original cell wall, intensive technological research in this field must be considered a logical development. However, it is not quite so clear why investigators have insisted that the results of such researches must have a bearing on the constitution of components of the lignin. The lignin derivatives in the waste liquor contain sulfur, and are apparently salts of sulfonic acids, although all of the sulfur is not bound in this stable form. They bear some resemblance to the tannins and some of the proximate groups present appear to be the same as those found in Willstatter lignin. These industrial products have been grouped together under the very elastic term *lignosulfonic* (or ligninsulfonic) acids.

Despite the immense amount of research lavished upon these products,<sup>10</sup> research that has been of marked technical importance, Pringsheim, one

<sup>10</sup> Cf. Johnsen and Hovey, "Utilization of Waste Sulfite Liquor," *Can. Forestry Branch Bull.* No. 66 (1919).

of the most astute workers in the field of polysaccharides and their related products, has said, "We cannot believe that a deeper insight into the nature of the lignin molecule will be gained by these studies (on the lignosulfonic acids)." Nevertheless, so many of the speculations regarding the "lignin molecule" have come as a direct result of just such studies that we may be warranted in describing the work in this field in some detail.

The difficulties under which investigators of sulfite liquors have worked are worthy of attention. Their concentrated spent sulfite liquor contained the lignin derivatives in the colloidal state, besides inorganic salts, and fermentable and unfermentable sugars obtained during the cooking operations. When precipitating agents, such as  $\text{CaCl}_2$  or  $\text{NaCl}$ , were used, a part of these lignin derivatives separated as amorphous precipitates, often quite difficult to filter, still more difficult to wash free from impurities, and frequently difficult to dry without change. Sometimes the lignin derivatives were isolated as lead salts, more frequently as sodium, calcium, or barium salts, sometimes as aryl amine derivatives, and at other times as the free sulfonic acids. Practically all of these products defied crystallization. The free acids always carried appreciable amounts of mineral matter. Investigators ordinarily had no criteria of the homogeneity or purity of their products other than the approximate constancy in analytical data obtained on these products after repeated fractional precipitation or dialysis. Under the circumstances, it is surprising that certain investigators have placed so much reliance on their calculated empirical formulas and that others had the temerity to express their results in terms of definite constitutional formulas, some of which have been all too readily accepted and copied by editors of technical publications and trade journals.

Probably the first investigator to suggest the presence of a calcium sulfonate in spent sulfite liquors was Pedersen,<sup>11</sup> and the first analyses of this rather questionable substance were reported by Lindsey and Tollens,<sup>12</sup> who assigned the empirical formula  $\text{C}_{24}\text{H}_{10}\text{O}_{12}\text{S}$  to the "free lignosulfonic acid" with the specific reservation that the uncrySTALLizable material from sulfite liquor might be heterogeneous and that the formula represented only the mean percentage composition. Lindsey and Tollens also raised the question as to whether or not the product from sulfite liquor was related to the tannins. They showed that although their product precipitated hide powder and gave an insoluble precipitate with lead acetate, it did not give the characteristic tannin reactions with iron salts.

<sup>11</sup> *Papierzeitung*, 15, 422 (1890).

<sup>12</sup> *Ann.*, 267, 341 (1892).

Shortly thereafter, Streeb<sup>13</sup> analyzed a barium salt of a lignosulfonic acid, which approached the empirical formula  $C_{56}H_{48}O_{22}S_2Ba$  and in which three methoxyl groups were apparently present. This corresponded to a formula of the "free acid" of approximately  $C_{14}H_{28}O_{11}S$ , a substance of much lower carbon content than those previously described. Streeb also obtained experimental evidence that the products from sulfite liquors were actually sulfonic acids. On heating with alkalis or alkaline earths the products were decomposed into the corresponding sulfites and "lignic acids" which closely resembled the products described by Lange.<sup>14</sup>

Seidel<sup>15</sup> some five years later showed that when he isolated the sulfonic acids from spent liquors of different sources, he obtained products which showed decided variations in percentage composition. One of his products approximated the empirical formula of the product previously described by Lindsey, but this may have been fortuitous.

Seidel's findings regarding the non-homogeneity of lignosulfonic acids were amply confirmed by Spitzer and Honig<sup>16</sup> who showed that a number of different lignosulfonic acids could be isolated from individual sulfite liquors. On concentrating the liquor *in vacuo*, freeing the "sulfonic acids" by means of  $H_2SO_4$ , and converting the acids into the barium salts, Honig and Spitzer were able to separate these compounds by fractional precipitation with alcohol. In this way they obtained at least three different fractions which were clearly differentiated by their different methoxyl content. To these fractions they assigned the formulas:  $C_{43}H_{50}O_{18}S_2Ba$ ,  $C_{40}H_{44}O_{18}S_2Ba$ , and  $C_{74}H_{114}O_{48}S_2Ba$ , at the same time frankly admitting that the fractions were not necessarily homogeneous compounds. It is interesting that the second barium salt tallied closely in percentage composition with a lignosulfonate described by Klason, and that all of the barium lignosulfonates<sup>17</sup> when heated with barium hydroxide for 4-6 hours yielded appreciable amounts of a substance which appeared to be homogeneous and the percentage composition of which indicated the formula,  $C_{17}H_{27}O_9(OCH_3)SBa$ . Judging by its color reactions and by its precipitation reactions, this substance was evidently related to the catechu tannins. Honig and Spitzer also found that all of their barium lignosulfonates yielded appreciable amounts of protocatechic acid when fused with alkali.

Melander's<sup>18</sup> painstaking work on sulfite liquor also indicates that different liquors yield different products and that a number of different lignin derivatives may be isolated from one individual spent liquor.

<sup>13</sup> *Mittheilungen K. techn. Versuchsanstalt*, Berlin, 11, 23, (1893).

<sup>14</sup> *Loc. cit.*

<sup>15</sup> *Mitt. Techn. Gew. Mus.*, 7, 119 (1897).

<sup>16</sup> *Monatsh.*, 39, 1 (1918).

<sup>17</sup> Cf. Honig and Fuchs, *Monatsh.*, 41, 215 (1920).

<sup>18</sup> *Cellulosechemie*, 2, 41 (1921).

Melander made use of NaCl in precipitating one of his lignosulfonate fractions. This material (a mixture of sodium salts) he converted into the free acid (which he attempted to purify) and also into derivatives of such organic bases as *o*-toluidine. After analyzing his various lignosulfonic acid fractions, calculating empirical formulas, and from these calculating the hypothetical sulfur-free lignin formulas,<sup>19</sup> Melander concludes that the lignins in the different fractions obtained from a single liquor have approximately the same percentage composition, but that the composition varies sufficiently to render it improbable that a homogeneous lignin derivative had ever been isolated. Differences between different lignosulfonic acid fractions became more striking when a number of different liquors were examined. "We must emphasize the fact," says Melander, "that calculated sulfur-free lignin formulas remain uncertain because of the complex, amorphous, and high molecular nature of the lignin." F. König<sup>20</sup> also points to the fact that lignosulfonic acid must be considered a heterogeneous mixture of related compounds, the percentage composition of which varies with the source of the liquor and the methods of isolation used. These results have been confirmed by other investigators.<sup>21</sup>

Despite the accumulating data in evidence of the non-homogeneity of "lignosulfonic acid," certain investigators have taken the stand that definite lignosulfonates can be isolated. Of these, Klason is perhaps the outstanding protagonist for the existence of homogeneous lignosulfonates. On the basis of his analytical data on the lignosulfonates, Klason has not only devised empirical formulas but *constitutional* formulas for the parent substance *lignin*. These constitutional formulas have changed from time to time to keep pace with Klason's accumulating experimental data.

Most of Klason's work was done on spruce lignin derivatives. His earlier work indicated that the barium salt of an individual lignosulfonic acid isolated from spent sulfite liquors approached the formula:  $C_{40}H_{42}O_{17}S_2Ba$ . Later<sup>22</sup> his investigations of a calcium lignosulfonate indicated that *this* compound had the formula:  $C_{40}H_{44}O_{18}S_2Ca$  and that the lignin (from which this was derived) was  $C_{40}H_{42}O_{12} \approx (C_{40}H_{44}O_{18}S_2Ca$  minus  $CaH_2S_2O_6$ ). On the basis of more intensive work, however, certain phases of which have already been discussed, Klason concluded that sulfite waste liquors contained two different lignin sulfonic acids.<sup>23</sup>

<sup>19</sup> Obtained by deducting the elements of ( $H_2SO_4$ ) sulfuric acid from the lignosulfonic acid formulas.

<sup>20</sup> *Cellulosechimie*, **2**, 94 (1921).

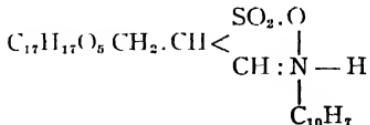
<sup>21</sup> Cf. McKee and Barsky, *Paper Trade J.*, **74**, 46 (May 18, 1922).

<sup>22</sup> *Arkiv. Kemi Min. Geol.*, **6**, Pt. 15, 7 (1917).

<sup>23</sup> Most investigators seem agreed that two different *types* of lignosulfonic acids exist. One type is readily precipitated by NaCl, CaCl<sub>2</sub>, and the aryl- and naphthyl-

one of which is precipitated by  $\text{CaCl}_2$  as the more common calcium lignosulfonate while the other is left in solution. The first of these, according to Klason, is identical with the substance precipitated as a yellow anhydro salt by means of  $\beta$ -naphthylamine.<sup>24</sup> This lignosulfonate appears to be the derivative of a lignin (termed "α-lignin" or "acrolein lignin") to which Klason assigned the formula  $\text{C}_{22}\text{H}_{22}\text{O}_7$  and which he believes has the  $-\text{CH}:\text{CH}-\text{CH}:\text{O}$  grouping. *A priori* on the basis of Klason's analyses the formula  $\text{C}_{20}\text{H}_{20}\text{O}_6$  (or  $\text{C}_{40}\text{H}_{40}\text{O}_{12}$ ) would appear more logical, but Klason on examining the sulfite liquors found that they contained approximately the amount of acetic acid that would account for *one* acetyl group in the original lignin. Furthermore on methylation of the "acrolein lignosulfonic acid" fraction, Klason finds that the per cent methoxyl has been increased in an amount that accounted for *one* free hydroxyl group. This is the hydroxyl group which Klason believes was acetylated in the original spruce (acrolein) lignin. Therefore, allowance for *one* acetyl group is made in Klason's acrolein lignin formula which instead of  $\text{C}_{20}\text{H}_{20}\text{O}_6$  becomes  $\text{C}_{20}\text{H}_{19}\text{O}_6(\text{O}-\overset{\underset{\parallel}{\text{O}}}{\text{C}}-\text{CH}_3)$ . Besides this, Klason's

acrolein lignin was believed to contain two methoxyl groups. In Klason's later work he replaced the rather unsatisfactory analysis of calcium acrolein lignosulfonate by analyses of the yellow  $\beta$ -naphthylamine derivatives of the sulfonic acid. They appear to substantiate his earlier findings. The sulfite liquor was fractionally precipitated with  $\text{NaCl}$  and a  $\beta$ -naphthylamine derivative prepared from each of four fractions, as well as from the original mother liquor. All of these fractions showed the same average composition of 63.97 per cent C, 5.39 per cent II, 5.73 per cent S, and 2.22 per cent N, figures which correspond very closely to those demanded by an empirical formula of  $\text{C}_{30}\text{H}_{29}\text{O}_8\text{SN}$  or



which is in harmony with the assumption that (deacetylated) acrolein lignin is  $\text{C}_{20}\text{H}_{20}\text{O}_6$ . The freshly precipitated  $\beta$ -naphthylamine derivative which is quite soluble in  $\text{CH}_3\text{OH}$  is said to crystallize from its methyl-alcoholic

amines. The other type is the more soluble, and remains in the mother liquors, which must be concentrated before the sulfonate can be isolated. Öman (*Papierfab.*, 14, 509 (1916)) has attempted to differentiate between these types by naming the former *lignansulfonic acid* and the latter the *lignonesulfonic acid*. There is no convincing evidence, however, to force the conclusion that either of these is a homogeneous substance.

\* Cf. Chap. 3 of this monograph.

solution, but Klason gives no analyses of the crystalline material. Klason also prepared the  $\alpha$ -naphthylamine and semicarbazide derivatives of acrolein-lignosulfonic acid. Analyses of these, roughly confirmed his empirical formula, as did the analyses of various salts. Molecular weight determinations of these salts, however, were not entirely satisfactory. The oxidation of calcium acrolein-lignosulfonate by perhydrol (30 per cent  $H_2O_2$ ) yielded a compound that could be precipitated with  $\alpha$ -naphthylamine and this precipitate had the percentage composition of  $C_{40}H_{16}O_{11}SN_2$  which indicated the introduction of two naphthylamine groups. Klason explained this oxidation by assuming that a *carbonyl* group had been converted into a *carboxyl* group and a methylene into a carbonyl group. Furthermore, acetylation of the original  $\alpha$ -lignosulfonic acid followed by saponification indicated that two hydroxyl groups had been originally present, and apparently one of these groups resisted methylation. Much of this experimental data is not very convincing. The homogeneity of the product formed by perhydrol is in doubt and the presence of two different types of hydroxyl groups, both of which can be acetylated and only one of which can be methylated, requires further confirmation.<sup>25</sup>

Klason's soluble lignosulfonate (which he considered a derivative of  $\beta$  or acrylic acid lignin containing the  $—C_11:CH—CO_2H$  group) was isolated as the calcium lignosulfonate from the mother liquors of  $\alpha$ -lignosulfonate (that had been previously removed by precipitation with  $\beta$ -naphthylamine).<sup>26</sup> In very concentrated solutions this  $\beta$ -lignosulfonic acid also combined with  $\beta$ -naphthylamine but with *two* molecules of *amine*. On the basis of this, Klason assumed both  $—SO_3H$  and a  $—CO.OH$  grouping in the compound which had the empirical formula:  $C_{30}H_{16}O_{10}N_2S$ . From this Klason formulated "acrylic acid lignin," the precursor of the sulfonic acid, as  $C_{10}H_{14}O_7$ . According to Klason, spruce wood contains acrolein lignin and acrylic acid lignin in the ratio of 2 to 1.

Klason also made some interesting attempts to synthesize the lignins. Coniferyl alcohol, he found, changed on standing, and the two products obtained were apparently the results of oxidation and polymerization. Both had approximately the same percentage composition as coniferyl aldehyde, but different molecular weights. One was apparently a dimer, the other a trimer of the aldehyde. Both had the same percentage composition as unacetylated acrolein lignin, to which the dimer seemed closely related. In fact, the only difference observed between the synthetic and the natural substance (according to Klason) is the inability of synthesized substance (termed "hemiacrolein lignin") to react readily with bisulfites.

On the basis of these, and other experiments, Klason attempted to

<sup>25</sup> Klason had assumed that one of these groups was alcoholic, the other phenolic in nature.

<sup>26</sup> *Ber.*, 56, 300 (1923).

show the relationship between coniferyl alcohol and the two lignins. A recent hypothesis assumed that acrolein lignin is a polymerization product of coniferyl aldehyde, while acrylic acid lignin may be a condensation product of coniferyl aldehyde with caffeic acid. This hypothesis, on the basis of later experiments, has been modified. Acrolein lignin<sup>27</sup> now appears to be a combination of three molecules of coniferyl aldehyde with one molecule of coniferyl alcohol. This would require that the formula of *deacetylated* acrolein lignin be doubled to C<sub>40</sub>H<sub>40</sub>O<sub>12</sub>.

Klason's work has been so widely quoted that it must be examined critically. In our opinion, Klason has placed too much confidence in the homogeneity of his products. He has always worked with large molecules, largely amorphous products, not with smaller, crystallizable decomposition products (obtained by mild hydrolysis, oxidation, etc.). In arriving at his formulas he consistently overlooks the fact that relatively small analytical differences in sulfur or nitrogen determination may affect his empirical formulas considerably, since the calculation of the empirical formula of a large molecule depends so much upon the accurate determination of those elements which occur in the smallest atomic ratios. Up to the present, none of his experimental data offer incontrovertible evidence that his working hypotheses or his constitutional formulas are correct. This is borne out by the rapidity with which Klason himself has modified his structural formulas.

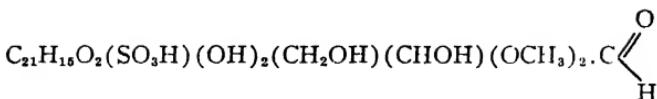
On the other hand, Klason's interesting pioneering work has greatly stimulated research on lignin and has been of immense practical value in standardizing the cooking operations in sulfite pulp manufacture. Furthermore, various observations made by Klason have been directly or indirectly confirmed by investigators like Hagglund.

A recent investigation by Dorée and Hall<sup>28</sup> on a lignosulfonic acid fraction obtained by the action of 7 per cent H<sub>2</sub>SO<sub>4</sub> on spruce wood at about 100° C. is of interest since it deals with a purified product and also assumes the homogeneity of the isolated lignosulfonic acid. In this case the liquor was subjected to a preliminary dialysis which removed H<sub>2</sub>SO<sub>4</sub>, hexoses, and pentoses, and which yielded a water soluble product C<sub>26</sub>H<sub>30</sub>O<sub>12</sub>S that strangely enough agreed in its empirical formula with the lignosulfonic acid fraction isolated by Lindsey and Tollens.

Dorée and Hall summarize their work by stating that the "persistence of the C<sub>26</sub> unit through all changes with a resistant nuclear unit of the order of C<sub>20</sub> leads . . . to the conclusion that the nucleus of lignone is hydroaromatic in character." Their product is reminiscent of the acrolein lignosulfonic acid described by Klason, and they give as their "dissected" empirical formula:

<sup>27</sup> Klason, *Ber.*, **58**, 375 (1925).

<sup>28</sup> *Chem. and Ind.*, **43**, 257 T (1924).



The evidence presented for the presence of some of these groups is rather scanty. For example, the "3 or 4 hydroxyl groups" are determined by the formation of the tri- or tetra-benzoate. A corresponding acetate could not be prepared and the analytical data presented in the case of the benzoate are inconclusive. The evidence that there are three different types of hydroxyl groups in their lignosulfonic acid (i.e., CHOII, CH<sub>2</sub>OH, and phenolic (?) OH) is based on still more questionable data. The action of 5 per cent HNO<sub>3</sub>, it is assumed, leads to (1) the removal of the sulfonic group as H<sub>2</sub>SO<sub>4</sub>; (2) to the oxidation of a CH<sub>2</sub>OII and a > C=O to corresponding carboxyl groups, (3) to the oxidation of a CHOII to a carbonyl grouping, (4) to the formation of "nitro compounds" and (5) to the loss of one methoxyl group. The compound thus formed, it is claimed, has the "dissected formula": C<sub>22</sub>H<sub>22</sub>O<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub>(OCH<sub>3</sub>)(CO<sub>2</sub>II)<sub>2</sub>(CO). On further treatment with 32 per cent nitric acid, oxidation proceeds further with the formation of a compound C<sub>22</sub>H<sub>24</sub>O<sub>12</sub>(NO<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>H). To the critical reader it appears that the experimental data are all too meagre to support these assumptions.

While Dorée and Hall's analytical results on the original dialyzed lignosulfonic acid agree very well with those required by their empirical formula, they admit that even their purified material carried as much as 6 per cent silicious ash. The analytical data recorded for certain of the derivatives of their lignosulfonic acid are certainly not convincing (e.g., the tribromo derivative, C<sub>20</sub>H<sub>20</sub>SO<sub>12</sub>Br<sub>3</sub>, the phenylhydrazine derivative of the nitro compound, etc.) and their "dissected formulas" rest upon interesting speculation rather than on the results of rigorous experimental work. Klason,<sup>27</sup> who has repeated Dorée and Hall's work, believes that their lignosulfonic acid was in fact a mixture of two acids derived from acrolein lignin: C<sub>40</sub>H<sub>10</sub>O<sub>12</sub>.2H<sub>2</sub>SO<sub>3</sub> and C<sub>40</sub>H<sub>40</sub>O<sub>12</sub>.H<sub>2</sub>SO<sub>3</sub>.

### **Physico-Chemical Studies on the Lignosulfonic Acids**

The dialysis experiments of Dorée and Hall recall that the physico-chemical character of sulfite liquor has been studied by various investigators. Samec and Rebek,<sup>28</sup> who had previously studied the mode of occurrence of H<sub>2</sub>SO<sub>3</sub>,<sup>29</sup> and the equilibrium existing between the chemically "bound" and chemically "free" H<sub>2</sub>SO<sub>3</sub> in sulfite liquors, have shown that on dialysis in parchment, sulfite liquor loses its free sulfurous

<sup>27</sup> *Kolloid Chem. Beihefte*, 19, 106 (1923).

<sup>28</sup> *Kolloid Chem. Beihefte*, 16, 215 (1922).

acid and any sulfites that are loosely bound to the lignin (to  $>\text{C}=\text{O}$  groups). The stable lignosulfonic acids are completely retained in the dialysis residue. Electrodialysis following dialysis effected the separation of a free lignosulfonic acid fraction in the middle compartment of the cell in which the acidity by titration corresponded almost exactly with the acidity as calculated from the sulfur content of the dried material. This material will presumably form the starting product for further investigation from the Laibach laboratories. Electrodialysis, however, also caused anodic oxidation, which was construed as evidence in favor of carbonyl groups in the lignosulfonates.

The difficulty in arriving at the approximate molecular weights of lignosulfonates becomes evident from the researches of Klason. In 1911, this investigator reported as a result of cryoscopic study that the approximate molecular weight of barium lignosulfonate was about 6,000. In 1917, he reported that the molecular weight of calcium lignosulfonate was 2,000 by the freezing point; about 1,000 by the boiling point method. Since then, both Melander and F. Konig have made independent critical studies of the molecular weight determinations as applied to the lignosulfonates. Melander<sup>31</sup> examined the so-called "lignin-S-acid," a fraction isolated from sulfite liquors by precipitation with NaCl, followed by isolation of the free acid. The equivalent weight of the acid was determined by gradual addition of NaOH with simultaneous determination of electrical conductivity. This equivalent weight corresponded almost exactly with the equivalent weight calculated from Melander's analytical data, and he concludes that the lignosulfonic acid is monobasic. He also showed that the sodium lignosulfonate was mappreciably hydrolyzed and concluded that it contained no *carboxyl* group. Melander's conclusions are that the molecular weight of the lignosulfonic acid is not a multiple of the equivalent weight, that this mean<sup>32</sup> molecular weight is about 680 from which the molecular weight of the precursor lignin (i.e., lignin-sulfonic acid *minus*  $\text{H}_2\text{SO}_4$ ) approaches 600. Melander also made determinations of the "thermodynamic" degree of dissociation ( $\gamma$ ) which in the case of the free acid ranged from 0.62 to 0.88 (as calculated from the determination of hydrogen-ion concentration, using the hydrogen electrode and dividing the H-ion concentration by the normality). From a study of electrical conductivity,  $\gamma$  ranged from 0.60 to 0.65. Apparently Melander also found that the degree of dissociation of sodium lignosulfonates over a wide range of concentrations resembled that of the free acid. Here the degree of dissociation varied from 0.63 to 0.79.

Konig<sup>33</sup> also studied the conductivities of solutions of free ligno-

<sup>31</sup> *Svensk Pappers-Tid.*, 24, 377 and 396 (1921); *C. A.*, 16, 4342 (1922).

<sup>32</sup> Mean molecular weight since the lignosulfonic acid is, of course, heterogeneous.

<sup>33</sup> *Cellulosechemie*, 2, 93 (1921).

sulfonic acid as well as those of a carefully purified barium lignosulfonate fraction (which of course was not considered homogeneous). The conductivity curve of the free lignosulfonic acid fraction showed marked similarities to that of  $H_2SO_4$ , including the usual maximum at a dilution of about 1 equivalent to 2,000 liters. This similarity with  $H_2SO_4$  was also indicated by decomposition voltages of barium and zinc lignosulfonates measured by Müller's method,<sup>34</sup> which gave the values 2.23 volts and 2.4 volts respectively. These values compared closely with those of the alkaline earth salts of a strong acid (= 2.2) and that of  $ZnSO_4$  (2.35 V). This also confirms Melander's finding that sodium lignosulfonate is unhydrolyzed. Konig's other results (on the salt of lignosulfonic acid) are not quite in harmony with those of Melander. The conductivity measurements on barium lignosulfonate give the extrapolated value  $\Lambda_\infty$  at  $18^\circ = 74$ . Deducting from this the migration velocity of the Ba-ion = 55, the migration velocity of the lignosulfonic acid ion at infinite dilution becomes 19 reciprocal ohms. This value does not check with the value of 9.3 mhos (at  $25^\circ$ ) found by Melander, and which, according to Melander, is an exception to Bredig's rule that mobility of ions approaches a minimal value of 17-20 when the molecule contains 50-60 atoms. However, so small a migration velocity is unique for both ions and colloidal particles, whose velocity according to Zsigmondy lies between 19.3 and 38.6. Konig explains the difference between his migration velocity and that found by Melander by pointing to the possible incorrectness of Melander's extrapolation. However, both Melander's results and Konig's indicate that the conductivity of the lignosulfonates increases more slowly with increasing dilution than in the case of other salts—until a certain point is reached, at which the conductivity increases more rapidly than is customary with other salts. Konig explains these abnormal conductivity curves by assuming that there are two sets of equilibria in solution of the lignosulfonates. Colloidal particles  $\rightleftharpoons$  molecules; molecules  $\rightleftharpoons$  ions. At those dilutions at which the free lignosulfonic acid solutions appear practically optically empty (i.e., in molecular or ionic form), the barium lignosulfonate still showed the presence of colloidal particles. According to Konig similar equilibria exist in sulfonates of high molecular weight like benzopurpurin and congo red.<sup>35</sup>

Assuming the correctness of Konig's hypothesis, the degree of dissociation of lignosulfonates cannot be accurately expressed by the ratio  $\frac{\Lambda}{\Lambda_\infty}$ . The true degree of dissociation is always much greater, although this does not seem to have been generally considered by other investigators.

Konig has pointed out that molecular weight determinations by boil-

<sup>34</sup> "Elektrochem. praktikum," p. 85 (1919).

ing point and freezing point methods in the case of lignosulfonates can only give approximate mean values. An error is introduced due to colloidal particles which have no appreciable effect on either elevation of boiling point or depression of freezing point. However, this error is in part compensated for by the fact that the degree of dissociation  $\frac{\Lambda}{\Lambda_\infty}$  is too low. So it may happen that the molecular weight calculated from analytical data may agree approximately with the molecular weight determined by other methods without, however, justifying the conclusion that lignosulfonic acid is monobasic.

Konig differs with Melander by assuming that the "lignosulfonic acid fraction" is mainly composed of dibasic acids. The similarity of the conductivity curves of  $H_2SO_4$  and of lignosulfonic acid, and the virtual impossibility of calculating even an approximate dissociation constant for lignosulfonic acid seem to justify this opinion.

### Summary

The analytical work on the lignosulfonates is briefly summarized in Table IX. The lignosulfonates all retain methoxyl and hydroxyl groups, and the sulfonic acid group is also invariably present. Regarding the nuclei present in the lignosulfonates, investigators have left us in much the same doubt that exists regarding the nuclei in the various lignin fractions. The fact that protocatechuic acid is obtained from lignosulfonic acid on fusion with alkali, and that the action of  $Ba(OH)_2$  on lignin yields an apparently homogeneous substance related to the catechol tannins, strongly suggests the presence of aromatic (or hydroaromatic) nuclei.

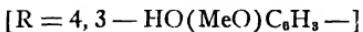
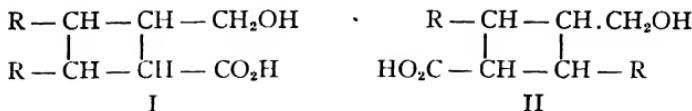
TABLE IX  
FORMULAS OF LIGNOSULFONATES DERIVED BY DIFFERENT INVESTIGATORS \*

Investigators	Composition of Lignosulfonate or Lignosulfonic Acid
Lindsey and Tollens . . . . .	$C_{10}H_{10}O_3S$
Streeb . . . . .	$C_{10}H_{10}O_2S_2Ba$
Seidel . . . . .	$C_{10}H_{10}O_3S$
	{ $C_{10}H_9O_2S_2Ba$
	$C_{10}H_9O_3S_2Ca$
Klason . . . . .	$C_{10}H_9O_2S_2Ca$ (acrolein lignin)
	$C_{10}H_{10}O_2SCa$ ( $\beta$ -lignin)
	{ $C_{10}H_9O_2S_2Ba$
	$C_{10}H_9O_3S_2Ba$
	$C_{10}H_{10}O_2S_2Ba$
Homig and Fuchs . . . . .	$C_{10}H_9O_2S_2Ba$
Konig . . . . .	$C_{10}H_{10}O_2S_2Ba$
Doree and Hall . . . . .	$C_{10}H_{10}O_2S$

\* Melander obtained such a large number of related sodium lignosulfonate fractions that these have not been included in the table.

### The "Sulfite Liquor Lactone"

The indefinite lignosulfonic acids, previously referred to, appear to be the principal components of waste sulfite liquor. However, when the spent liquors (after cooking spruce wood) are extracted with ether or benzol, a definite compound appears in the extract. Holmberg<sup>45</sup> by means of immiscible solvents obtained less than 0.1 per cent of a lactone,  $C_{20}H_{20}O_6$ , melting at 250-5°, containing 2 methoxyl groups, which could be converted into the corresponding hydroxy acid ( $C_{20}H_{22}O_7$ ) melting 172-3°,  $[\alpha]_D^{18} 75^\circ$ , which in turn reverts very readily into the lactone. Holmberg, has described a number of derivatives of the acid, including an *amide*, melting at 139-40°,  $[\alpha]_D 85^\circ$  (in acetone) and a *diacetyl derivative*  $C_{24}H_{24}O_8$ , melting at 221-2°,  $[\alpha]_D - 73.5^\circ$ ; a *monosulfoxyl derivative*  $C_{20}H_{22}O_6S$ , melting at 172-3°, and two *bromo derivatives*. The lactone sublimes at about 220-30° with little change but when heated above its melting point or on treatment with sodium ethylate it is apparently converted into an isomer, melting at 210-11°. Phenylhydrazine and semicarbazide have no action on the lactone, which, however, couples readily with diazobenzidine. Ammoniacal  $AgNO_3$  is reduced by the lactone. Fehling solution remains unaffected. Strong oxidizing agents yielded only oxalic acid. Dimethylsulfate yielded a *dimethyl lactone*, silky crystals, melting at 179-80° and containing *four* methoxyl groups. This dimethyl derivative is converted, in part, into an *isomeric dimethyl lactone* (melting about 145°) on heating. Both of the dimethyl derivatives formed corresponding crystalline hydroxyacids. While phloroglucinol and hydrochloric acid gave no coloration with the lactone, the reagent gives a cherry red coloration with alkaline solutions of lactone, oxidized in air. All of Holmberg's carefully purified products were crystalline, their molecular weights could be accurately determined and the analytical data are in close accord with his theoretical calculations. On the basis of his experiments Holmberg assigned either Formula I or II to the hydroxy acid from which the original sulfite liquor lactone is derived. He considers this an inner anhydride of diguaiacoltetramethylenecarbinol carboxylic acid. How closely the lactone is related to other lignin derivatives in waste liquor has not been determined.



<sup>45</sup> *Svensk Kem. Tidskrift*, 32, 56 (1920); *Ber.*, 54, 2389, 2406 (1921).

Hintikka<sup>36</sup> applied Holmberg's procedure to birch and aspen woods, but failed to obtain any product analogous to the lactone, which may serve to characterize the liquors of coniferous woods.

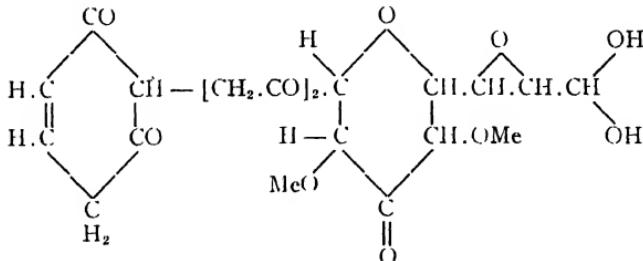
### Speculations on the Constitution of Lignin<sup>37</sup>

Despite the limitations of experimental data on lignin, various investigators have presented tentative constitutional formulas for lignin—usually applying these to the lignin of spruce wood.

The stimulus that such formulations have given to lignin research have been overshadowed to a certain degree by the fact that the formulas are based on insecure or fragmentary evidence. *We must stress the fact that all constitutional formulas for lignin are premature* and it is for this reason that little space can be devoted to them.

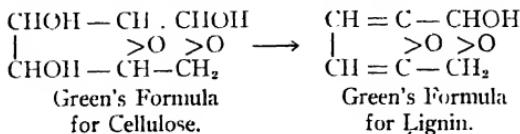
Some of the more stimulating constitutional formulas that have been proposed are:

1. The Cross and Bevan formula,<sup>38</sup> which assumes a "keto-R-hexene" ring joined to a hydrogenated pyrone ring containing two methoxyl groups. This was applied to the "lignocellulose" of jute and obviously lacks supporting experimental data.



Cross and Bevan's Formula for the "Lignone" in "Lignocellulose."

2. Green's formula, which assumes the conversion of cellulose molecules into lignin molecules by loss of water.<sup>39</sup> This formula is no longer in harmony with all the experimental data on cellulose.



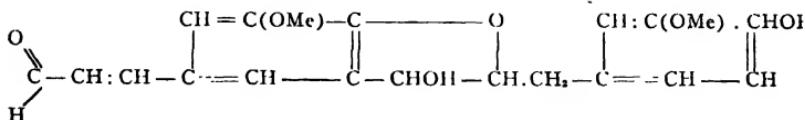
<sup>36</sup> *Cellulosechemie*, 2, 87 (1921).

<sup>37</sup> For reviews on this subject, cf. Schwalbe, "Chemie der Cellulose"; Fuchs, *Ber.*, 54, 484 (1921); Riefenstahl, *Z. angew. Chem.*, 37, 169 (1924).

<sup>38</sup> "Cellulose," p 137, "Researches on Cellulose," III, 104.

<sup>39</sup> *Z. Farben Textilchemie*, 3, 97 (1904).

3. Klason's various lignin formulas, all of which assume that coniferin (via coniferyl alcohol and its derivatives or oxidation products) plays a rôle in the synthesis of  $\alpha$ - and  $\beta$ -lignin.

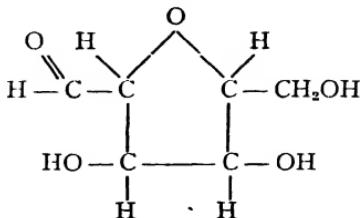


Klason's Formula for "Unacetylated"  $\alpha$ -Lignin.<sup>40</sup>

4. Schrauth's "partial formulation" ("abgerundetes Bild") of lignin which cleverly correlates and harmonizes what appear to be conflicting observations on the chemistry of lignin.<sup>41</sup>

Schrauth assumes, *a priori*, that lignin possesses a molecular complexity analogous to that of the proteins or tannins, and that lignin isolated by the methods previously described is no longer identical with the substances present in the cell wall. Isolated lignin fractions probably represent smaller fragments resulting from the partial degradation of a larger molecule (or aggregate), the true structure of which cannot be explained in the light of our present knowledge. In his formulation, Schrauth balances the results of those experiments which point to an aromatic or hydroaromatic nucleus in lignin (as indicated by the work of Klason, Ilonig, Pictet, etc.) with those which point to the aliphatic origin of lignin (as indicated by Willstatter, Jonas, von Marcusson, etc.).

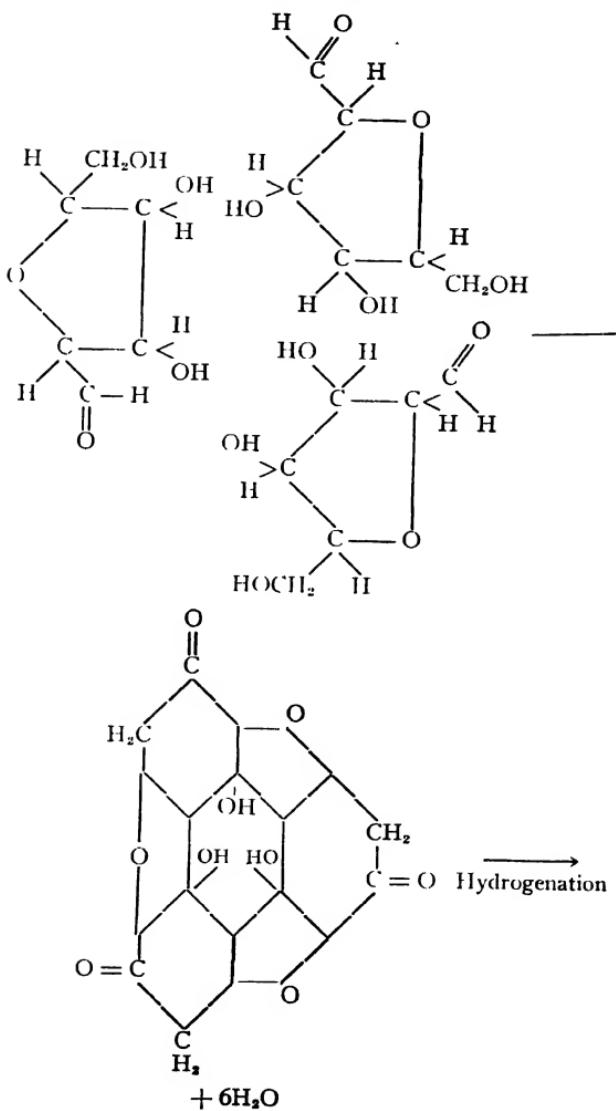
Schrauth points to the fact that carbohydrates, especially glucose under specific conditions (such as treatment with strong acids), yield 5-hydroxy-methyl furfural, with the elimination of water. As a precursor of this product, a hypothetical substance would be one having the structure:

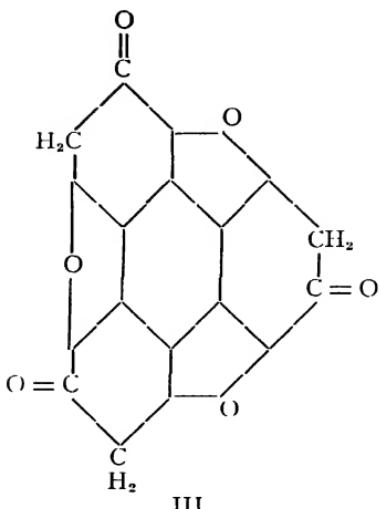


in which the water has not yet been eliminated. Assuming that three such molecules can condense with elimination of water, Schrauth proposes the following reaction:

<sup>40</sup> Ber., 56, 300 (1923).

<sup>41</sup> Z. angew. Chem., 36, 149 (1923).





The above compound then contains three furan rings and is also a hydroaromatic substance ( $C_{18}H_{18}O_6$ ) which through the reducing action of the plant life process may be converted into a compound in which the central three OH groups are reduced, giving a compound of the formula  $C_{18}H_{18}O_6$  (Formula III). The compound contains the active  $-CH_2-C-$  grouping, which can also take the enolic form:

$$\begin{array}{c} \text{O} \\ || \\ -\text{CH}=\text{C}-\text{OH}. \end{array}$$
 The latter has the capacity of forming esters and

ethers, and may account for the presence of methoxyl derivatives in lignin. A lignin molecule of this type would also be capable of forming derivatives with simple sugars or polysaccharides that would resemble the tannins. Nitration should yield compounds similar to the nitrophenols and oxidation should cause a rupture of the  $-CH_2-C=O$  groups,

with formation of high molecular hydroaromatic carboxylic acids (humic acids) which would finally give benzolpolycarboxylic acids similar to those reported by Fischer and Schrader.<sup>42</sup> A deep-seated hydrogenation should yield perhydrogenated hydrocarbons (similar to those reported by Willstatter and Kalb<sup>43</sup>) which, if degradation (Zersplitterung) has not

<sup>a</sup> Loc. cit.

<sup>b</sup> Loc. cit.

taken place, would have molecular weights of 246 or 490, or some approximate multiple of these figures which is in harmony with Willstätter and Kall's results. Willstätter's reduction might well be accompanied by a series of condensations since hydroaromatic ketones, and especially cyclohexanone and its homologs, are susceptible to autocondensation to bi- and tricyclic products (in presence of acids and alkalis and by means of heat and pressure).<sup>44</sup> A simple picture of this type of condensation would be represented by formula IV on p. 94.

A substance of this type could, of course, readily be converted to alkyl (methyl) ethers through the enolic form of the  $> C = O$  grouping. An hypothesis of this sort also appears to be in harmony with analytical data obtained on isolated lignin fractions. As an example, a lignin isolated from coniferous wood meal by Willstätter's method by Fischer and Schrader<sup>45</sup> contained 13.1 per cent MeO. However, the authors showed that 22 per cent of the MeO originally present in the wood was lost during the acid treatment required in the isolation. Let us assume (with Schrauth) that this 22 per cent was present in the lignin of the original wood and that the lignin isolated had the formula on p. 95 (*minus 22 per cent MeO*):

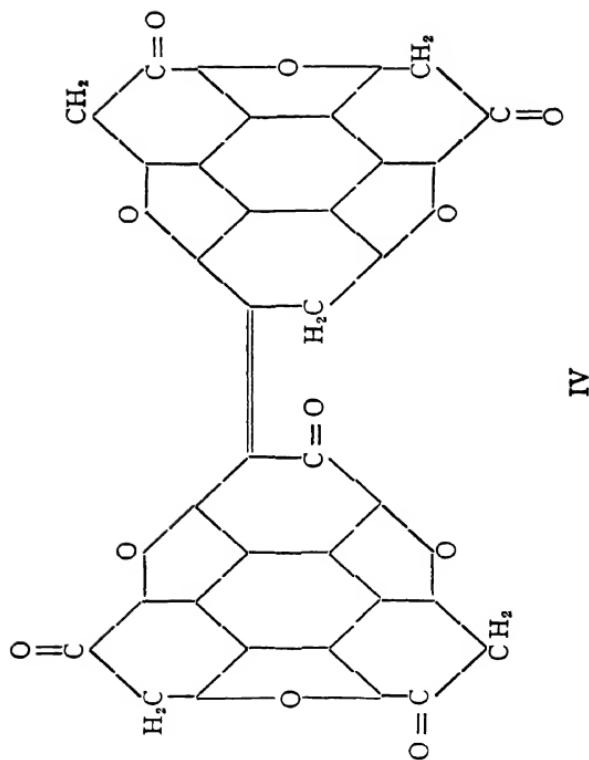
Then the following figures of Fischer and Schrader are in striking agreement with the ones calculated on the basis of such an hypothesis.

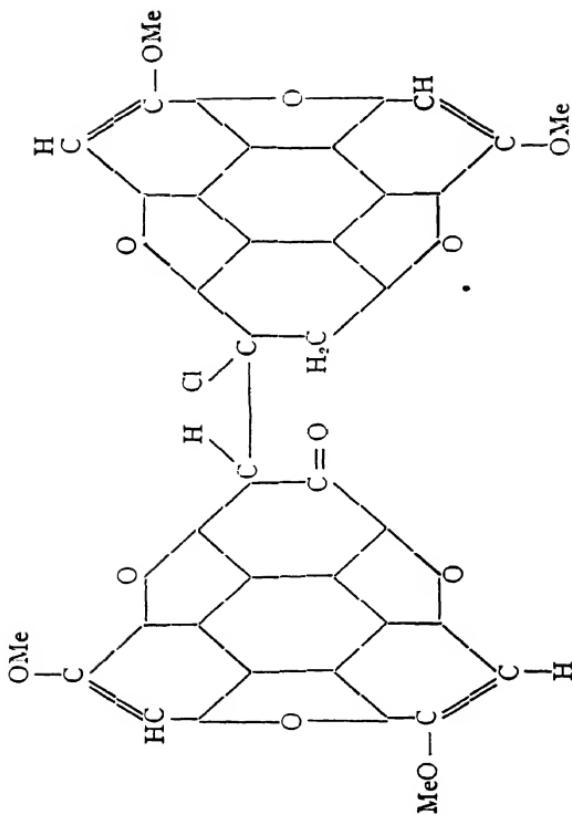
	Per Cent C	Per Cent H	Per Cent MeO
Calculated	64.98	5.75	13.3
Found by F and S.	64.79	5.65	13.1

However (in disagreement with Pringsheim), Schrauth believes that the explanation of lignin structure cannot be obtained as readily from isolated lignin, as from a study of the lignosulfonic acids resulting in the sulfite cooking process and previously referred to. If Schrauth's hypothesis is correct, formation of such sulfonic acids would have to be explained satisfactorily by his formulas (III or IV), taking into consideration the reaction caused in the cooking process.  $Ca(HSO_4)_2$  probably does not act as a condensing agent to the same degree that a strong mineral acid (used in isolating lignin) would act. Assuming that in a simple molecule of the type of formula III two carbonyl groups react in the enolic form and are methylated, the theoretical formula for the calcium lignosulfonate would be  $C_{40}H_{46}O_{18}S_2Ca$ . If, however, a condensation has occurred as in the case of formula IV (followed or preceded by methylation) the simplest Ca lignosulfonate becomes  $C_{40}H_{44}O_{17}S_2Ca$ . Calculated per cent C, H, O, S, Ca, and OMe for either of these two

<sup>44</sup> Wallach, *Ber.*, **40**, 70 (1907).

<sup>45</sup> *Ges. Abhandl. Kennt. Kohle*, **5**, 108 (1920).





possibilities agree reasonably well with the best figures for calcium lignosulfonate obtained by Klason and by Honig and Spitzer, although the latter assume as the most probable formulas:  $C_{40}H_{42}O_{18}S_2Ca$  and  $C_{40}H_{44}O_{18}S_2Ca$  for their lignin fractions. However, as these investigators make no claim for the homogeneity of their Ca salts, these salts may be varying mixtures of the two possibilities outlined by Schrauth.

Klason's  $\beta$ -lignin  $C_{10}H_{18}O_7$  (acrylic acid lignin) is also accounted for by Schrauth's formulations, provided we assume that in formula III the  
$$\begin{array}{c} \text{---C---CH}_2\text{---} \\ || \\ \text{O} \end{array}$$

life process—with the formation of  $CO_2H$  groups. However, Schrauth admits that Klason's  $\beta$ -lignin requires further study before its constitution can even be guessed at intelligently.

Schrauth's ingenious speculations should prove decided stimuli to further investigation in the lignin field.

## Chapter 5

### Extraneous Components of Wood

The term "extraneous components" has been devised to include a number of substances, present in some woods, absent from others, which are often grouped together under the general designation of "*extractives*" These substances while present in the woody tissue (*xylem*) can usually be extracted by means of suitable solvents. They are therefore not considered an integral part of the cell walls of the wood. Needless to say, however, there are numerous borderline cases in which it is impossible to state definitely whether or not a substance is actually part and parcel of the cell wall. The authors, then, are cognizant of the limitations of their own definition.

Not a few of these extraneous components have a decided commercial value. Some few of them are responsible for tropical industrial diseases. Others have a marked scientific interest to the phytochemist and plant physiologist. Often their true origin and biochemical significance is obscure. The authors have made the deliberate attempt to avoid an exhaustive discussion of the extraneous components of *all* woods. They have chosen what they consider striking examples of such components and have attempted to give references to comprehensive articles or monographs relating to the subject matter in this chapter.

#### **The Tannins<sup>1</sup>**

The tannins hold an important place among the components of wood. The term *tannin* applies to those compounds which have the following general characteristics:

- (a) an astringent taste.
- (b) the property of yielding dark blue or greenish colorations with ferric salts.
- (c) the property of forming precipitates with various proteins (gelatin and albumin) and with certain alkaloids.
- (d) the property of converting hide into leather.

Furthermore, all tannins contain certain aromatic nuclei.

<sup>1</sup>A. G. Perkin and Arthur E. Everest, "The Natural Organic Coloring Matters"; Thorpe's Dictionary of Applied Chemistry, V, p 383.

The tannins are very widely distributed, occurring in many different woods, but comparatively few of these tannins have been intensively studied, and their chemical constitution is still unknown.

Nearly all tannins can be extracted from wood by means of hot water, and are therefore considered extraneous substances which do not form an integral part of the cell walls of woody tissue. When treated with lead acetate, the water extracts of the tannins yield precipitates from which the tannins may be regenerated by removing the lead with hydrogen sulfide. In the purification of the tannins fractional precipitation with lead acetate is often resorted to. Organic solvents are also frequently and very effectively employed in extracting tannins from plant tissues.

According to the classification of Perkin and Everest, the tannins found in wood (and hitherto investigated) would fall into (a) the *depside* group and (b) the *catechol* or *phlobatannin* group. The tannins of class (a) give bluish-black colors or precipitates with ferric alum. On heating at 160-215° they yield pyrogallol. Some of them contain the glucose nucleus in the tannin molecule.

A tannin of class (a) is found in Spanish chestnut wood (*Castanea vesca* Gartn.) (*C. sativa* Mill.) and serves as a raw material for the production of chestnut extract. This tannin is closely related, if not identical, with the important "gallotannin" (ordinary tannin) found in gall nuts, which result from the puncture by insects of leaves and twigs of various oaks. The tannin in gall nuts has been subjected to a series of careful investigations, among which the works of E. Fischer and Freudenberg must be cited. They showed that gallotannin is probably a penta-*m*-digalloylglucose.<sup>2</sup>

Another tannin, probably belonging to class (a), is *quercin*, which is found in the wood of oak. This is a pale brownish substance,  $C_{15}H_{12}O_6 \cdot 2H_2O$ , which was investigated by Bottinger.<sup>3</sup> It has been confused with, but is quite distinct from the tannin found in oak barks (*quercitannic acid*) which belongs to the above mentioned groups of phlobatannins, class (b).

These phlobatannins yield green colorations with ferric salts and give distinctive red precipitates when heated with aqueous mineral acids. These red substances are known as anhydrides or "phlobaphenes." An attempted differentiation between the phlobatannins and the depsides which depends on the fact that the former give rise to catechol or protocatechuic acid on decomposition is misleading. Some phlobatannins exist which do not yield catechol.

A tannin belonging to the phlobatannin group is present in the ("ax-breaking") wood of "*quebracho colorado*" (*Loxopterigium Lorentzii*

<sup>2</sup> *Ber.*, **45**, 915 and 2709 (1912); **46**, 1116 and 3253 (1913); **47**, 2485 (1914).

<sup>3</sup> *Ber.*, **20**, 761 (1887), *Ann.*, **263**, 110 (1890).

Griesb.). The tannin content of this wood may exceed 20 per cent,<sup>4</sup> but there is some evidence that quebracho tannin is not homogeneous.<sup>5</sup> On dry distillation it yields catechol. Among the products of alkaline fusion are phloroglucinol, protocatechuic acid and resorcinol.

Closely related to the catechol tannins (and also to the natural dye-stuffs) is *acacatechin*, a substance found in the heartwood of *Acacia Catechu* Willd. It is isomeric but not identical with *catechin* isolated from the gambier bush. Acacatechin is a crystalline compound,  $C_{15}H_{14}O_6 \cdot 3H_2O$ , melting at 204-5° C., yielding pentaacetyl and benzoyl derivatives and giving phloroglucinol and protocatechuic acid on fusion with alkali.<sup>6</sup>

According to Czapek<sup>7</sup> large quantities of tannins are not infrequently found in old wood (of the heartwood). Here the oxidation products of the tannins may play a rôle in the formation of the dark or highly colored substances so often present in heartwood. The possible relationship between the tannins and lignin has been touched upon in a previous chapter.

Moureu<sup>7a</sup> has suggested that phenolic substances, especially the tannins may play the rôle of antioxidants. Apparently the life of the plant is least intense, where they occur in largest amount. This suggestion of Moureu, while an interesting working hypothesis, demands further experimental evidence before it can be accepted.

Within recent years, the tannin contents of a number of American woods have been determined. Benson and Jones<sup>8</sup> found that the wood of Douglas fir (*Pseudotsuga taxifolia*), western larch (*Larix occidentalis*) and western yellow pine (*Pinus ponderosa*) contained appreciable amounts of tannin (6-10 per cent), while western hemlock wood (*Tsuga heterophylla*) (whose bark is rich in tannin) yielded only 1 per cent tannin. On storage, the tannin content of Douglas fir increased (from about 6 per cent tannin to 7.5 per cent tannin). Wood of dogwood (*Cornus Nuttallii*); cottonwood (*Populus trichocarpa*); and alder (*Alnus oregonia*) all contained appreciable amounts of tannin (5-7 per cent). While tannin extracts of the foregoing coniferous trees and of dogwood may be commercially valuable, the tannins of the cottonwood and alder appear to have little economic significance. An analysis of redwood (*Sequoia sempervirens*)<sup>9</sup> by Scalione and Merrill showed that the sapwood contained 1.15 per cent tannin, while the heartwood contained over 12 per

<sup>4</sup> Proctor, "Leather Manufacture" (1922), p. 306, Moeller, *Collegium* (1920), 106.

<sup>5</sup> Nierenstein, *Collegium* (1905), 65

<sup>6</sup> Perkin and Everest, *loc. cit.*, p. 471

<sup>7</sup> "Biochem. Pflanzen," III, 510

<sup>7a</sup> *Compt. rend.*, 174, 258 (1922).

<sup>8</sup> *J. Ind. Eng. Chem.*, 9, 1096 (1917)

<sup>9</sup> *J. Ind. Eng. Chem.*, 11, 643 (1919)

cent of tannins. Since the investigations of Wilson and Kern<sup>10</sup> have recently shown that the official method of the American Leather Chemists Association for tannin determination is inaccurate, it is probable that the above results are all far too high.

### The Natural Dyestuffs and Their Precursors \*

While the coloring principles and dyes in plants are usually associated with the leaf and the flower, and are largely absent from fruits, roots, bark, and wood, there are cases in which the woody tissue is unusually rich in these substances. Classical examples are the brazilwoods and logwood, and other examples, such as the wood of "old fustic," osage-orange, and young fustic, might be cited. Some of the dyestuffs thus obtained from wood are still commercially valuable, although the importance of others has receded with the growth of the synthetic dye industries.

In many cases the dye itself is not preformed in the wood, and its precursor (i.e., the coloring principle) may be extracted from the finely divided wood by means of ether, alcohol, or water, or by a succession of solvents. The coloring principles are therefore not a part of the cell wall but must be grouped with the extraneous substances of wood.

The most important commercial dyestuff is obtained from logwood (Campeche wood, *Hæmatoxylon campechianum* L.), a tree which is indigenous to South America and the West Indies and which belongs to the *Cesalpinae* group of the *Laguminosæ*. The coloring principle, *hæmatoxylin*, may be extracted from the finely divided wood by means of ether, or may be isolated from concentrated (aqueous) logwood liquor on slow evaporation, followed by extraction with ether, and repeated crystallization from water. Prepared in this way it forms prismatic crystals containing 3 molecules of water of hydration. Its molecular formula was shown by Erdmann<sup>11</sup> and later by Hesse<sup>12</sup> to be C<sub>16</sub>H<sub>11</sub>O<sub>6</sub>. As a result of extensive investigations a number of different structural formulas representing *hæmatoxylin* have been proposed.<sup>13</sup> The constitutional formula accepted by W. H. Perkin and his co-workers after a series of extensive researches and by Pfeiffer<sup>14</sup> on theoretical grounds is given below.

<sup>10</sup> *J. Ind. Eng. Chem.*, 12, 465 and 1149 (1920); 13, 772 (1921), *J. Am. Leather Chem. Assoc.*, 15, 451 (1920).

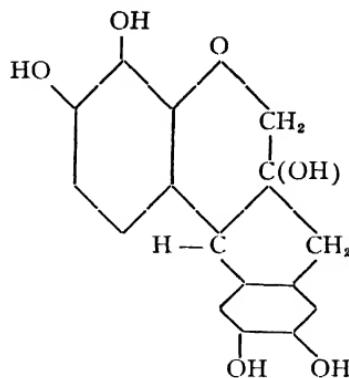
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<sup>11</sup> *J. prakt. Chem.*, 26, 193 (1842), 75, 218 (1858).

<sup>12</sup> *Ann.*, 109, 332 (1859).

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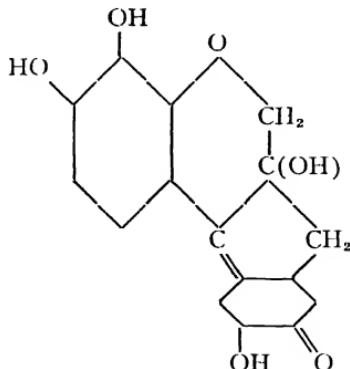
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*Haematoxylin*

Oxidation of haematoxylin causes its conversion into the actual coloring matter *haematein* in accordance with the following equation:



This oxidation results when logwood is "aged" or when ammoniacal logwood extract is exposed to the air. Haematein apparently has the structural formula given below:

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Logwood is widely used in producing "blacks" on wool, silk and (to a lesser extent) on cotton. It is one of the few natural dyestuffs that has withstood the competition of the synthetic dyes.

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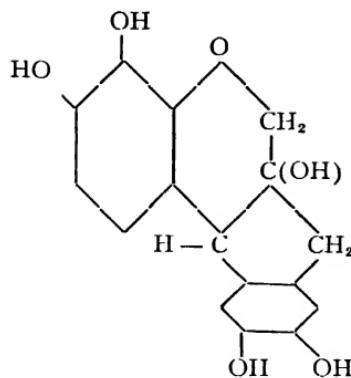
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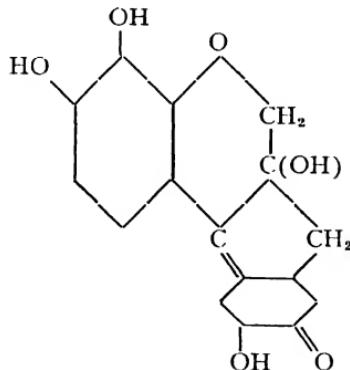
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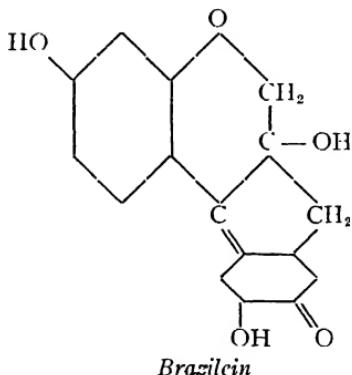
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Closely related to logwood are the so-called "soluble redwoods" grouped together under the collective term "Brazilwood." All of them belong to the Caesalpinaeæ and they have a rather wide distribution.\*

The coloring principle present in these woods is termed *brazilin* ( $C_{16}H_{14}O_5$ ) and crystallizes in colorless needles or prisms from water. It is chemically very closely related to the *haematoxylin* of logwood. On oxidation it gives rise to the actual dyestuff *brazilein* which dissolves in alkalis with a deep red color that is destroyed by excessive oxidation.



Interesting work leading to a formulation of the constitution of brazilein has been carefully reviewed by Perkin and Everest. Apparently the coloring matter of logwood is a *hydroxybrazilein*, and *brazilein* itself appears to have the following structure:



The redwood dyestuffs still enjoy a limited utilization in printing calico and in wool dyeing—but the colors are not very fast and have been largely replaced by the synthetic dyes.

Another dyewood related to brazilwood is *Haematoxylon africanum* found in Great Namaqualand in S. Africa. Its characteristic coloring principle resembles *brazilin* rather closely but it has no technical importance.

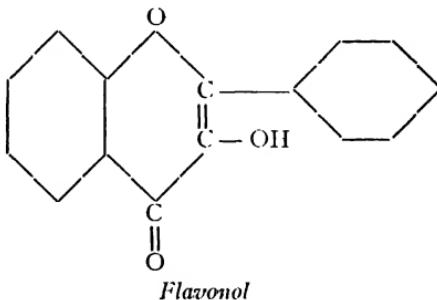
Besides the "soluble" redwoods (i.e., the Brazilwoods, etc.) there are a number of different woods containing red dyestuffs of unknown composition, which are but slightly soluble in water. These are known as

\* Pernambuco wood, which is probably richest in coloring matter, is found in *Caesalpinia Crista* L. in Jamaica and Brazil. The true "Brazilwood," *C. brasiliensis* L. (which probably gave Brazil its name because of its "fiery red" (*brazo*) dyewood) is found only in that country. Sappanwood (*C. Sappan* L.) is found in certain parts of Asia, and a variety of this (Limewood) is grown in the Philippines. Peachwood (*C. echinata* Lam.) is indigenous to Central America and to parts of South America.

the "insoluble redwoods" and yield dyestuffs that dissolve in alcohol and which are used to a very limited extent as direct substantives for wool.

Four of these "redwoods" may be grouped together. Sanderswood (Santalwood) is a product of *Pterocarpus santalinus* L., a tree growing in the East Indies. It contains the coloring matters *santalilin* ( $C_{24}H_{22}O_8$ ) and *dcooxysantalin* ( $C_{24}H_{24}O_7$ ). Barwood (*Baphia nitida* Lodd.) is found on the West African coast. It is possible that this wood contains some of the same components that are present in sanderswood, although chemical data are still incomplete. Narrawood (*Pterocarpus spp.*), native to the Philippines, contains the dark red dyestuff, *narrin*, which appears to be similar to but not identical with *santalilin*. Camwood (or cambe wood) which may be a variety of *Baphia nitida* contains the dyestuffs *isosantalin* ( $C_{22}H_{16}O_6(OMe)_2$ ) and *dcooxyisosantalin*, which while very similar to *santalilin* and *dcooxysantalin* respectively, show different color reactions and are characterized by different dyeing properties.

A number of yellow dyestuffs obtained from several different species of wood belong to the *flavonol* group:



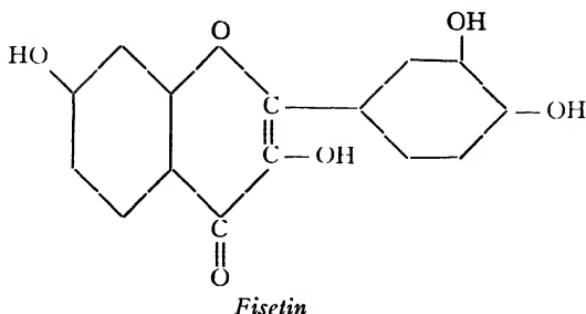
Among these is "young fustic," the wood of the *Rhus Cotinus* L. indigenous to Southern Europe and the West Indies, which has little commercial value as a dyewood. Its yellow coloring matter consists of fisetin, to which Herzig<sup>15</sup> assigned the structure of a *trihydroxyflavonol*.

Besides fisetin, young fustic also contains a glucoside of fisetin, apparently combined with a tannic acid (fustin tannide).<sup>16</sup> Fisetin is also present in yellow cedar wood (*Rhodospheara rhodanthema* Engl.) and in *quebracho colorado*.\*

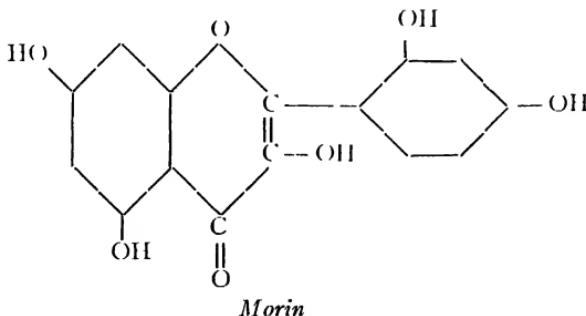
<sup>15</sup> *Monatsh.*, 12, 178 (1892).

<sup>16</sup> Schmid, *Ber.*, 19, 1734 (1886).

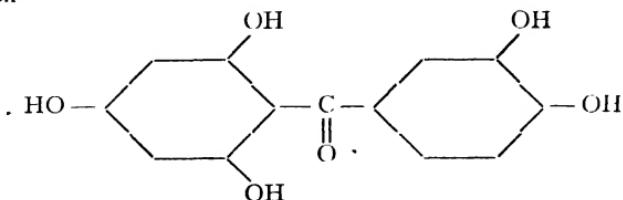
\* Fisetin closely resembles quercetin, the coloring matter of the inner bark of *Quercus discolor* Ait, which is a monohydroxyfisetin (*i.e.* a tetrahydroxyflavonol). Quercetin is also present in *Acacia Catechu*.



A Cuban dyewood, known as "old fustic," occurring in *Chlorophora tinctoria* Gaudich., contains two dyes, *morin* and *maclurin*. Morin,  $C_{15}H_{10}O_7 \cdot 2H_2O$ , forms colorless needles from dilute alcohol and gives a yellow coloration with alkalis. The constitution of *morin* was shown to be that of a tetrahydroxyflavonol.<sup>17</sup>



*Maclurin*,  $C_{15}H_{10}O_6$ , is a pentahydroxybenzophenone, having the constitution<sup>18</sup>



<sup>17</sup> Bäblich and Perkin, *J. Chem. Soc.*, **69**, 792 (1896), Kostanecki, Lampe and Tambor, *Ber.*, **39**, 625 (1906), Herzog and Hofmann, *Ber.*, **42**, 155 (1909).

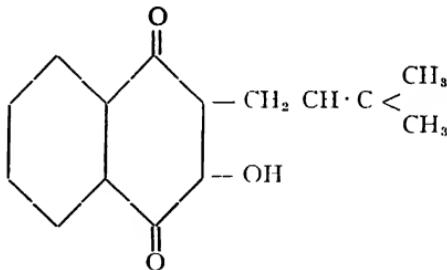
<sup>18</sup> König and Kostanecki, *Ber.*, **27**, 1996 (1894), Perkin and Robinson, *Proc. Chem. Soc.*, pp 22 and 305 (1906), Kostanecki and Tambor, *Ber.*, **39**, 4022 (1906).

Old fustic is probably the most important of the natural yellow dyes used in coloring wool. On the other hand, its use in dyeing silk and cotton is quite limited. When the woolen fabric is mordanted with chromium ( $K_2Cr_2O_7$ ) or with copper or iron salts, old fustic yields colors that are exceeding fast to light. The dye is often used in conjunction with other dyestuffs in the formation of olive drabs and brown colors.

An American dyewood, which apparently contains both morin and maclurin, is produced by the osage orange tree (*Maclura pomifera*, Schne.), a native of Texas, Arkansas and Oklahoma.<sup>19</sup> The dye, which was used for many years by the native Indians, served as a substitute for "old fustic" during the War, and was employed in leather and textile dyeing, and is still used in the leather industry.

Jackwood (*Artocarpus integrifolia*, Linn) grows in India and is used in dyeing the silken garments of the priests of Burma. It also contains the dyestuff morin, but not maclurin. Another substance, known as *cyanomaclurin*, is also present in Jackwood. This compound,  $C_{15}H_{22}O_6$ , crystallizes in colorless prisms and when dissolved in hot aqueous alkali gives rise to a rich indigo-blue coloration. Aqueous extracts of Jackwood possess this same property.

An interesting substance which occurs in the heartwood of *Avicennia* and in the wood of various members of the *Bignoniaceae* family is *lapachol*, a golden-yellow crystalline quinone, melting at approximately 140° C. and shown by Hooker<sup>20</sup> to have the following constitution



This compound may be so abundant in the xylem, that the wood has the appearance of having been dusted with powdered sulfur.<sup>21</sup> A dilute caustic soda solution imparts a characteristic pink color to woods containing lapachol. Record claims that the presence of lapachol in a "wood of

<sup>19</sup> Kressman, Yearbook, U. S. Dept. of Agriculture, 1915, p. 201.

<sup>20</sup> J. Chem. Soc., 61, 611 (1892), and 69, 1355 (1896).

<sup>21</sup> Record, *Tropical Woods*, Tropical Series No 1, p. 7 (1925).

"normal structure" may be taken as fairly conclusive evidence that it belongs to the Bignoniaceæ—although the absence of the compound cannot be used as an indication that the wood does not belong to this group.

From the preceding brief description of the dyewoods, it will be noted that the commercially valuable coloring principles present in wood fall largely into two general classes: (1) those related to dihydropyran and (2) those related to flavonol. The insoluble redwoods contain dye-stuffs of unknown constitution. Dyewoods of other types also exist but they possess little if any industrial value.

### Carbohydrates in Wood

The non-sugar polysaccharides of wood have been previously discussed and their occurrence in wood substance proper and as extraparietal components has been noted.

The living cells of the wood (i.e. the wood ray and longitudinal parenchyma cells) act as storage elements for the so-called "reserve" polysaccharides present in sapwood. The dead cells (*prosenchyma*) apparently never store reserve foodstuffs, although they may act temporarily as viaducts in the transportation of solutions of the sugars.

Simple sugars and complex sugars are therefore probably present as extraneous substances in various parts of the woody tissue, although the individual identification of these sugars is not an easy matter, nor one which has engaged the attention of many chemists. If our generally accepted theories regarding the synthesis of starch and cellulose can carry any weight, glucose must be present in wood. Its presence is also indirectly indicated by the seasonal disappearance of starch in the wood which probably results from the enzymatic hydrolysis of starch to maltose and dextrose. Critical experimental data, however, are meager and Czapek<sup>22</sup> has pointed out that a careful experimental study of the synthesis of reserve carbohydrates in wood has never been reported.

Unfortunately, tests for the presence of glucose in wood have depended largely on reduction experiments which might serve equally as well to indicate the presence of other reducing substances.<sup>23</sup> In most cases, the wood itself has not been examined but the presence or absence of various free sugars was gauged by an examination of the sap, or from a chemical examination of young twigs. In the case of twigs, it is always problematical whether the sugars are present in the wood or in the bark.

On the basis of such examinations, the sapwood of various American maples must contain sucrose. According to Wiley, "pure" maple saps contain no reducing sugars<sup>24</sup> but may contain up to 5 per cent sucrose.

<sup>22</sup> "Biochemie der Pflanzen," I, p. 477.

<sup>23</sup> Linsbauer, *Sitzber. Wien Akad.*, 129, Pt I, 215 (1920).

<sup>24</sup> *Chem. News*, 51, 88 (1885).

The sap of white birch was shown by Lenz<sup>25</sup> to contain fructose but no glucose. Apparently the fructose content varies between 0.3 and 2.0 per cent.<sup>22</sup> Wislicenus, however,<sup>23</sup> states that birch sap contains both fructose and sucrose. The trisaccharide, raffinose, was found by Herissey and Lefébre<sup>24</sup> in young twigs of various species of Taxaceæ and of certain other conifers. The presence of this same sugar had been shown in the manna of the Tasmanian *Eucalyptus mannifera* Mudie before the middle of the 19th Century.<sup>25</sup> A manna coating the surface of twigs of Douglas fir (*Pseudotsuga taxifolia*) consists largely of the trisaccharide *melezitose*<sup>26</sup> and forms an excellent source of supply for this rare and interesting sugar.

Among the extraneous substances whose presence in wood has been reported sporadically are the glucosides. Normally compounds of this type are found in the cambial sap, in the bark, leaves, etc., but their positive identification in the xylem is fraught with experimental difficulties and uncertainties. Coniferin (which has been previously discussed) probably occurs in the young wood of a large number of conifers although its presence in older woody tissues has been reported on insufficient experimental evidence.<sup>40</sup> The enzyme *emulsin* hydrolyzes coniferin to glucose and coniferyl alcohol. Fustin, the glucoside in fustic wood (*Rhus Cotinus* L.) has already been alluded to in another section. On hydrolysis it yields rhamnose and fisetin (a trihydroxyflavonol). It is quite probable that glucosides related to fustin occur in other woods. Shibata, Nagai and Kishida who have examined the leaves, flowers, bark and wood of more than 240 tropical plants, found that flavone derivatives were always present. In many instances such derivatives were probably in the form of glucosides.<sup>51</sup>

### The Oleoresins, Resins, and Essential Oils<sup>52</sup>

Normally, the term "oleoresin" refers to a viscous mixture of a non-volatile solid substance and a liquid essential oil, *secreted* by the resin forming cells of the sapwood when the tree is wounded by scarifying, boring, etc. The term "resin" is applied to the resinous material *actually present* as an extraneous substance in the wood proper. There is no very

<sup>25</sup> *Ber. pharm Ges.*, **19**, 332 (1909).

<sup>22</sup> Czapek, *loc. cit.*

<sup>23</sup> *C. Ulosochemie*, **6**, 50 (1925).

<sup>24</sup> *J. Pharm. Chim.* (6), **26**, 56 (1907).

<sup>25</sup> Thorpe's Dictionary, Vol I, p 654

<sup>26</sup> Hudson and Sherwood, *J. Am. Chem. Soc.*, **40**, 1456 (1918).

<sup>27</sup> Czapek, "Biochem. d. Pflanzen," Vol I, p 464

<sup>51</sup> *J. Biol. Chem.*, **28**, 93 (1916), Armstrong, "The Simple Carbohydrates and Glucosides."

<sup>52</sup> A comprehensive work on resins is that of A. Tschirch, "Die Harze und Harzbehalter" (1906). An excellent résumé of recent resin investigations (through

logical reason for calling this substance a *resin* rather than an *oleoresin*, since it also consists of an admixture of non-volatile materials and essential oils. It is important to note, however, that an oleoresin and a resin derived from the same tree are not necessarily identical in composition. The relative ease with which the resins may be extracted from wood makes it apparent that they do not form an integral part of the cell wall. This is also evidenced by microscopic examination. Both oleoresins and resins are usually soluble in ether and benzol and practically insoluble in water. They are frequently, though not always, soluble in alcohol.

The oleoresins and resins derived from the pines are of marked interest since they form the raw materials of the naval stores and resinous wood distillation industries. The principal oleoresin used in the naval stores industry is that obtained from longleaf pine (*Pinus palustris*) or the Cuban or slash pine (*P. heterophylla*).<sup>\*</sup> This consists of the non-volatile substance, rosin, and a volatile or essential oil, turpentine.

Rosin consists largely of *rosin acids* which have been subjected to extensive study but which still present a very difficult field for the investigator. These rosin acids probably belong to the two groups:<sup>13</sup> (1) the *abietic acid group*, members of which when treated with sulfur yield *retene*, and (2) a group of which *pimaric acid* is an important member and which, on dehydrogenation, gives rise to a hydrocarbon  $C_{16}H_{14}$  (possibly, dimethyl phenanthrene). The great difficulty in studying and identifying the rosin acids is that the physical properties of the isolated material are frequently influenced by the methods used in purification.

The formula of abietic acid has been variously given as  $C_{19}H_{24}O_2$  and  $C_{20}H_{30}O_2$ , with experimental data favoring the latter.<sup>14</sup> Knecht and Hibbert<sup>15</sup> and later Steele<sup>16</sup> have offered evidence that abietic *anhydride*

(1923) is given in Meyer and Jacobson, "Lehrbuch d. Organischen Chemie," Vol II, "Cyclische Verbindungen-Naturstoffe," part IV (1924), pp 125-180. Important books on essential oils include

"Chemistry of Essential Oils," Vols I and II (Van Nostrand, 1918-1919), by E. J. Parry.

"Semi-Annual Reports," Schimmel & Co

Scientific and Industrial Bulletins, Roure-Bertrand Fils, Grasse.

"Volatile Oils" (Wiley, 1913-6), Gildemeister and Hoffmann, translated by Kremers.

"Die Aetherischen Öle," F. W. Semmler.

"Terpene und Camphor," O. Wallach.

\* Synonyms or colloquialisms applied to these oleoresins are "gum," "crude turpentine," "dip" or "scrape," the two latter depending on whether the oleoresin is *dipped* from vessels into which the oleoresin flows, or *scraped* from the scarified face of the sapwood. The volatile portion of this oleoresin is often termed "oil of turpentine," "spirits of turpentine" or simple "turps." The non-volatile material is called colophony as well as rosin.

<sup>13</sup>Cf Rau and Simonsen, *Indian Forest Records*, XI, Pt VI, 207 (1924).

<sup>14</sup>Schorger, *U. S. Forest Serv. Bull.* 119, 8.

<sup>15</sup>J. Soc. Dyers Colour, 35, 149 (1919).

<sup>16</sup>J. Am. Chem. Soc., 44, 1333 (1922).

is actually present in the rosin but this is denied by Schorger.<sup>37</sup> Besides the abietic acid, small amounts of alkali-insoluble materials are present and these are termed *resenes*.

The volatile oil, turpentine, consists of hydrocarbons of the terpene series ( $C_{10}H_{16}$ ). Of these  $\alpha$ -*pinene* is the principal component and besides this there are present smaller amounts of  $\beta$ -*pinene* and *camphene*. The presence of other hydrocarbons has been suggested but not proved.<sup>38</sup>

Apparently oil of turpentine from longleaf pine is normally dextro-rotatory. That from slash pine shows levorotation.<sup>39</sup> In commercial samples these oils are present in admixture since the oleoresins are indiscriminately mixed when the collection is made. The physical properties of freshly prepared American turpentine may, therefore, vary considerably as indicated by the following data.<sup>40</sup>  $n_D^{20}$  1.4667—1.4722,  $\alpha_D^{20}$  34.8° to +29.6° (with the more common range from -2° to +20°),  $d_{20}^{20}$  0.858—0.876. In general the initial boiling point of turpentine oil is between 156° and 160°, and 90 per cent or more of the oil usually distills below 175°.

The resin present in the heartwood of old stumps of longleaf pine (termed "lightwood") is quite different in its nature from that of the oleoresin. The wood rosin is physically quite distinct from the "gum" rosin (of the oleoresin) and the essential oil in the resin shows marked chemical differences from that in the oleoresin. It contains not only the hydrocarbons  $\alpha$  and  $\beta$ -*pinene* and *camphene*, but also *l-limonene*, *dipentene*, and  $\gamma$ -*terpinene*, oxygen derivatives of the type  $C_{10}H_{14}O$ , including *cineol*, *i-fenchyl alcohol*, and  $\alpha$ -*terpineol* (a major component) and *l-borneol*, as well as *camphor* ( $C_{10}H_{16}O$ ) and *methylchavicol* ( $C_{10}H_{12}O$ ). Of these components, all the oxygen derivatives excluding cineol have boiling points above 200° C. and thus characterize the "wood oil" of longleaf pine, (known commercially as "pine oil").<sup>41</sup>

While the differences between "gum" and "wood" turpentine are usually quite marked, the turpentine obtained from sapwood (of freshly cut longleaf pine) is strikingly similar in composition to that isolated from the corresponding oleoresin. This was indicated by Hawley<sup>42</sup> who showed that the boiling point, specific gravity, and index of refraction curves of two such turpentines were very similar. (These curves were obtained by determining the physical constants of fractions obtained on distillation)

<sup>37</sup> *J. Am. Chem. Soc.*, **45**, 1339 (1923).

<sup>38</sup> Gildemeister and Hoffmann, 2nd Edition Translated by Kremers. Vol II, pp. 22-6.

<sup>39</sup> Herty, *J. Am. Chem. Soc.*, **30**, 866 (1908).

<sup>40</sup> Allen's "Commercial Analysis" (4th Edition), Vol IV, p. 406.

<sup>41</sup> Gildemeister and Hoffmann, "Volatile Oils," translation by Kremers (1916), p. 102.

<sup>42</sup> *Forest Service Bulletin*, **105**, 54 (1913).

Comparatively few researches have been instituted on the nature of essential oils present in the *resins* of American woods. Schorger has given a résumé of the literature in this field.<sup>43</sup>

The following wood oils were prepared by Adams<sup>44</sup> by carefully distilling wood under diminished pressure. Western yellow pine (*Pinus ponderosa* Laws) yielded an oil,  $d_{15}$  0.8626,  $n_D^{15}$  1.4727,  $\alpha_D^{20}$  — 13.15°, 97.7 per cent of which boiled below 181°. Its components consisted of *l*- $\alpha$ -*pinene*,  $\beta$ -*pinene*, and *limonene*. Jeffrey pine (*Pinus Jeffreyi*) yielded an oil,  $d_{15}$  0.677,  $n_D^{20}$  1.389 which was optically inactive and which consisted almost entirely of *n-heptane*. The wood of singleleaf nut pine (*P. monophylla*, Torr) gave an oil,  $d_{15}$  0.9702;  $n_D^{15}$  1.4771,  $\alpha_D^{20}$  + 21.15°, consisting largely of *d*- $\alpha$ -*pinene* and *cadinene*. It is interesting to note that these oils isolated from the wood itself correspond rather closely in composition with those obtained from the oleoresins secreted by the living tree (Cf. Table X).

The oil isolated from red cedarwood (*Juniperus virginiana* L.) by distillation, is a product of the waste of the pencil manufacturing industries. The American oil shows the following physical properties:<sup>45</sup>  $d_{15}$  0.940 — 0.944;  $[\alpha]_D$  — 40 to — 46°. Components of the German oil were investigated by Semmler<sup>46</sup> and his co-workers. These included the sesquiterpene, *cedrene* ( $C_{16}H_{24}$ ), an alcohol, *cedrenol* and a saturated alcohol, *pseudocedrol* ( $C_{16}H_{26}O$ ). *Cedrol* (an alcohol stereoisomeric with *pseudocedrol*) may also be present in shavings that have been in contact with air for a protracted length of time.

Schorger's investigations on the oil obtained by distilling the wood of Port Orford cedar (*Chamaecyparis Lawsoniana*)<sup>47</sup> may be summarized as follows:  $d_{15}$  0.891;  $n_D^{15}$  1.476;  $\alpha_D^{25}$  39.6°. The rectified oil contained approximately 60 per cent *d*- $\alpha$ -*pinene*, 6-7 per cent *dipentene*, 11 per cent *d-borneol*, 11.5 per cent *bornyl acetate*, 6-7 per cent *cadinene*, and small amounts of *acetic* and *capric acids*.

An interesting resin, extracted from the wood of southern cypress (*Taxodium distichum*) by means of alcohol was examined by Odell.<sup>48</sup> When subjected to fractional vacuum distillation the resin yielded two substances: an oil, *cypral*,  $b_{15}$  182-5°;  $d_4^{20}$  0.9469;  $n_D^{20}$  1.5040, which was probably an aldehyde, and greenish yellow viscous *sesquiterpene, cypressene* ( $C_{16}H_{24}$ )  $b_{15}$  218 — 20°  $d_4^{18}$  0.9647;  $n_D^{22}$  1.524.

Grimal<sup>49</sup> isolated an oil by distilling African sandarac wood (*Callitris*

<sup>43</sup> Contributions to the Chemistry of American Conifers, *Trans. Wisc. Acad. Sci. Arts and Letters*, 19, Part II.

<sup>44</sup> *J. Ind. Eng. Chem.*, 7, 957 (1915).

<sup>45</sup> Gildemeister and Hoffmann, Vol. II, 165.

<sup>46</sup> *Ber.*, 40, 3521 (1907), 45, 355, et al. (1912).

<sup>47</sup> *J. Ind. Eng. Chem.*, 6, 631 (1914).

<sup>48</sup> *J. Am. Chem. Soc.*, 33, 755 (1911).

<sup>49</sup> *Compt. rend.*, 139, 927 (1904).

*quadrivalvis* Vent) which contains phenols, consisting in part of *carvacrol* and *hydrothymoquinone*. The property of resisting the inroads of the wood destroying white ants (termites) possessed by the wood of various species of Australian *Callitris*, is presumably also due to the phenolic content of similar oils.

Much more work has been done on the oleoresins of the various conifers than on the wood resins. The results of some of this work can probably best be summarized in tabulated form. Table X includes only a fraction of results obtained in this field and should not be taken as a complete summary. (For details regarding the turpentine derived from various European and Asiatic pines, the reader is referred to Kremer's translation of Gildemeister and Hoffmann's monograph, Vol. II, pp. 69-87.) In general, the hydrocarbons present in the essential oils are terpenes, less frequently the sesquiterpenes and in rare cases the aliphatic hydrocarbons. In many instances the non-volatile portions of the oleoresins closely resemble gum rosin obtained from longleaf and slash pine, although proof is not at hand that the principal substances in all rosins are identical or even isomeric with abietic acid.

Schorger has pointed out that there are over 90 species of conifers in the United States. Only a comparatively small number of the oleoresins and resins obtained from these have been examined and yet these studies, limited as they are, have furnished some interesting and suggestive data. The same is true of Simonsen's excellent work on the oleoresins of Indian pines.

As an example, Schorger's work has actually aided in the identification of species.<sup>60</sup> He has shown that while botanists have had difficulty in identifying forms of pine, apparently intermediate between *P. ponderosa* and *P. Jeffreyi*, these "cross varieties" must be classified with *P. ponderosa*. Jeffrey pine is characterized by the presence of the aliphatic hydrocarbon *n-heptane*, in the oleoresin. (On the other hand, neither western yellow pine nor any of the "cross varieties" (so-called) yield this product.

Another instance in which the chemist has served the forester in his tree classification is that of *P. ponderosa* and *P. ponderosa var. scopulorum*. Foresters and botanists have sought to combine these two varieties. It is evident, however (Table X), that the component oils of the two types of oleoresins are quite dissimilar. Hence it seems reasonable to retain *P. ponderosa var. scopulorum* as a distinct variety of pine. Examples of this type should become more numerous with future investigations and the field offers a fascinating outlook for the phytochemist.

The occurrence of *n-heptane* and of *n-undecane* (normal components of American petroleum) in certain pine oleoresins has led Simonsen to a brief speculation on the possible origin of petroleum oils. Since some

<sup>60</sup> Proc. Soc. Am. Foresters, 11, 33 (1916).

TABLE X

DATA ON OLEORESINS OF VARIOUS AMERICAN AND INDIAN PINES

Tree	Components of the Volatile Oil	Physical Constants of the Oil	Notes on the Rosin of the Oleoresin	References
<i>Pinus Jeffreyi</i> (Jeffrey pine)	Largely <i>n</i> -heptane <i>n</i> -decyl aldehyde, limanol, methylchavicol as minor components.	$d_{15}^{20}$ , 0.6951-0.711 $n_D^{20}$ , 1.3927-1.4060 B <sub>pt</sub> (92.5%) 98.2- 113° C.	Resin crystallizes readily. Contains 12.5% resin. Resin acids appear to be iso- meric with abietic acid.	Schorger, <i>J. Ind. Eng. Chem.</i> , 5, 971 (1913). Schiimmel & Co. Reports (Oct. 1914- April 1915), p. 45.
<i>P. monophylla</i> (Singleleaf pine)	85% <i>d</i> - $\alpha$ -pinene 4-5% <i>i</i> - or <i>l</i> -limonene 4-6% cadinene	$d_{15}^{20}$ , 0.8721-0.8733 $n_D^{20}$ , 1.4732-1.4733 [ $\alpha$ ]D <sub>20</sub> <sup>a</sup> + 14.4 to 17.3°	Resin acids present are ap- parently isomeric with abietic acid, 7.2%. Resene present.	Schorger, <i>ibid.</i>
<i>P. sabiniana</i> Dougl. (Digger pine)	Almost entirely <i>n</i> -hep- tane.	$d_{15}^{20}$ , 0.6971 $n_D^{20}$ , 1.3903 B <sub>pt</sub> (95%) 96.1- 98.8° C	No crystalline acids obtained from original rosin. On dis- tillation under 10 mm. pres- sure yields crystals m. 151- 2°.	Schorger, <i>For. Ser. Bull.</i> , 119, 18 (1913).
<i>P. lambertiana</i> Dougl. (Sugar pine)	70-75% <i>d</i> - $\alpha$ -pinene 5% $\beta$ -pinene 2-3% of a terpen- 10-12% of a sesquiter- peno. Aliphatic hydrocar- bon(?)	$n_D^{20}$ , 1.4727-1.4728 [ $\alpha$ ]D <sub>20</sub> <sup>a</sup> + 10.42° $d_{15}^{20}$ 0.8663-0.8658	Rosin yields no crystalline compounds.	Schorger, <i>ibid.</i> , p. 22.
<i>P. ponderosa</i> Laws (Western pine)	5% <i>l</i> - $\alpha$ -pinene 60% <i>l</i> - $\beta$ -pinene 20% <i>l</i> -limonene 10% sesquiterpene (= cadinene <sup>b</sup> )	$d_{15}^{20}$ 0.8625-0.8688 $n_D^{20}$ , 1.4772-1.4793 [ $\alpha$ ]D <sub>20</sub> <sup>a</sup> — 12.4 to — 26.5	Contains 90% abietic acid	Schorger, <i>ibid.</i> , p. 11.
<i>P. ponderosa</i> <i>scopulorum</i> . Engelm. (Western yellow pine)	60-70% <i>d</i> - $\alpha$ -pinene 5% $\beta$ -pinene 20-25% limonene	$d_{15}^{20}$ 0.8639-0.8672 $n_D^{20}$ , 1.4723-1.4729 [ $\alpha$ ]D <sub>20</sub> + 12.86 to 13.03	Largely abietic acid.	Schorger, <i>ibid.</i> , p. 15.

<i>P. contorta</i> Loud. (Lodgepole pine)	Almost entirely <i>l</i> - $\beta$ -phellandrene	$d_{10}^{20}$ 0.8518-0.8549 $n_D^{20}$ 1.4860-1.4862 $[\alpha]_D$ — 20 12°	Largely abietic acid.	Schorger, <i>ibid.</i> , p. 25.
<i>P. edulis</i> Engelm. (Pifion pine)	70-75% <i>d</i> - $\alpha$ -pinene 5% $\beta$ -pinene 15-20% <i>d</i> -cadinene	$d_{10}^{20}$ 0.8680 $n_D^{20}$ 1.4707 $[\alpha]_D$ — 19 26°	Crystals obtained from crude oleoresin m. 137° (from MeOH and HCl). Isomeric with abietic acid.	Schorger, <i>ibid.</i> , p. 28.
<i>P. clausa</i> Sarg. (Sand pine)	10% <i>l</i> - $\alpha$ -pinene 75% <i>l</i> - $\beta$ -pinene 10% <i>l</i> -camphene	$d_{10}^{20}$ 0.8725 $n_D^{20}$ 1.4768 $[\alpha]_D$ — 22.5°	Largely abietic acid.	Schorger, <i>J. Ind. Eng. Chem.</i> , 7, 321 (1915).
<i>P. longifolia</i> Roxb.	<i>l</i> - $\alpha$ -pinene <i>l</i> - $\beta$ -pinene <i>d</i> - $\Delta^3$ -carene <i>d</i> -longitoline	$d_{10}^{20}$ 0.8717 $n_D^{20}$ 1.4725 $[\alpha]_D$ — 27.2°	70% rosin in oleoresin.	Simonsen and Rau, <i>J. Chem. Soc.</i> , 117, 570 (1920); Simonsen, <i>ibid.</i> , 123, 549 (1923); Simonsen, <i>ibid.</i> , 123, 2642 (1923).
<i>P. Khasaya</i>	<i>d</i> - $\alpha$ -pinene <i>d</i> - $\beta$ -pinene <i>d</i> -longitoline	$d_{10}^{20}$ 0.8633 $n_D^{20}$ 1.4675 $[\alpha]_D$ — 32.83°	60% rosin in oleoresin.	Simonsen and Rau, <i>Indian Forest Records</i> , 9 (Part IV), 112 (1922).
	<i>d</i> - $\alpha$ -pinene <i>d</i> -terpinol <i>n</i> -undecane sesquiterpene	$d_{10}^{20}$ 0.8575 $n_D^{20}$ 1.4627 $[\alpha]_D$ + 40.42°	68% rosin in oleoresin.	Simonsen and Rau, <i>ibid.</i> , p. 116.
	<i>d</i> - $\alpha$ -pinene <i>d</i> - $\beta$ -pinene <i>d</i> - $\Delta^3$ -carene <i>d</i> -longitoline; <i>l</i> -limonene;	$d_{10}^{20}$ 0.8575 $n_D^{20}$ 1.4653 $[\alpha]_D$ + 28.67°	69% rosin.	Simonsen, <i>Indian Forest Records</i> , 10 (Part IV), 51 (1923).
<i>P. Geraniana</i>	<i>d</i> - $\alpha$ -pinene (73%) <i>d</i> - $\beta$ -pinene Unidentified sesquiterpene, b. 157°, $n_D^{20}$ 1.4947. Unidentified sesquiterpene alcohol	67% rosin.	$d_{10}^{20}$ 0.8658 $n_D^{20}$ 1.468 $[\alpha]_D$ + 18.4°	Simonsen, <i>ibid.</i> , 9 (Part VIII), 345 (1923)

remains of coniferæ are present in early strata, it might appear that in certain areas at least these could perhaps have been sources of petroleum. Simonsen suggests that it would be desirable to carefully examine oils from some of the more primitive conifers such as the *Araucaria*.

Among the essential oils obtained from the wood of tropical broad leaved trees, sandalwood oil and oil of camphor deserve special if brief mention. Sandalwood (*Santalum album*, Linn.) is indigenous to India. The chipped wood when subjected to steam distillation yields (in European practice) as much as 6 per cent of an oil, 90 per cent of which consists of a mixture of two isomeric alcohols,  $\alpha$ - and  $\beta$ -*santalol*.<sup>51</sup> Besides this mixture, the following components are also present in Indian sandalwood oil: *isovaleric aldehyde*, *santene*, *santenone*,  $\pi$ -*norisoborneol*, *teresantalol*, *nortricyclocksantalal*, *santalone*, a ketone  $C_{11}H_{10}O$  (isomeric with *santalone*?),  $\alpha$ -*santalene*, *teresantalic acid*, and *santalic acid*. Although the oil was probably not isolated from sandalwood by the ancients, it was the odor of this oil which caused the wood to be so highly prized in ancient India and China where its utilization depended upon its durability and fragrance. In modern times the oil has played a rôle in medicine, in the treatment of genito-urinary diseases and diseases of the respiratory organs. Its medicinal properties are correlated with its santalol content.

Camphor oil<sup>52</sup> is a product of the wood of the camphor laurel (*Cinnamomum Camphora*, F. Nees). The character of the oil varies considerably and on fractionation the crude oil yields (1) a light camphor oil,  $d_{15}$  0.86-90, b. 175-200°; (2) a heavy oil,  $d_{15}$  (approximately) 0.95, b. 270-300°; and (3) a blue camphor oil,  $d_{15}$  0.95-0.96, boiling above 300°. The lowest fraction finds an application in the manufacture of varnishes and as a cleanser for printing presses. The intermediate fraction also finds a use in the varnish industry and in perfuming cheap soaps.

The following compounds (besides the characteristic component camphor) may be present in camphor oil: *acetic aldehyde*,  $d$ - $\alpha$ -*pinene*, *camphene*, *d-fenchene*,  $\beta$ -*pinene*, *phellandrene*, *cineol*, *dipentene*, *d-limonene*, *borneol*, *terpineol*, *terpinen-1-ol*, *citronellol*, *safrol* (which is present in large amounts),  $\Delta'$ -*menthene-3-one*, *carvacrol*, *cuminic alcohol*, *eugenol*, *bisabolene*, *cadinene*, *caprylic acid*, an acid ( $C_9H_{16}O_2$ ) and the "blue oil," b. 280-300°.

Oil of copaiba is obtained from an oleoresin elaborated by a number of species of *Copaifera* (family Leguminosæ) indigenous to certain parts of South America. The oleoresin ("balsam") collects in cavities of the tree trunk and exists abundantly in schizogenous ducts in the sec-

<sup>51</sup> Semmler, *Ber.*, **40**, 1120 (1907); **41**, 1488 (1908); **42**, 584 (1909); **43**, 1893 (1910).

<sup>52</sup> Details of the production of the oil are given in Gildemeister and Hoffmann's monograph (translation), Vol. II, p. 447, etc.

ondary wood. Pressure exerted by the oleoresin is sometimes so great that it bursts the trunk of the tree. The oleoresin yields from 30 to 80 per cent of volatile oil.<sup>53</sup> The characteristics of copaiba oil vary greatly with the locality in which the tree is grown. An oil from Maracaibo "balsam" ( $d_{15}$  0.9036;  $[\alpha]_D$  — 9°) contained  $\alpha$ - and  $\beta$ -*caryophyllene* and *l-cadinene* but other sesquiterpenes may also have been present. The oil is a mild stimulant, laxative, and diuretic and is used in the treatment of genito-urinary diseases and bronchitis.

Guaiac wood oil is obtained from the wood of *Bulnesia Sarmienti*, Lor. It contains a sesquiterpene hydrate, *guaiol*, and is used in perfumery to produce a tea-rose odor and as an adulterant of the costly oil of rose.

### Fixed Oils and Fats

Fixed oils are seldom associated by the chemist with the woody portion of the tree. On the other hand, it has been shown by phytochemists that during the winter months, reserve carbohydrates (like starch) which are present in the xylem are quite frequently converted into fats or oils in the living tree. The starch grains seem to disintegrate into miniature granules and oily droplets appear in their stead. The change may be followed microchemically by the gradual disappearance of the starch-iodide reaction and the appearance of a positive reaction for fats with osmic acid.<sup>54</sup> These fats or oils must, therefore, be considered typical reserve food stuffs of the stems of woody plants.

A. Fischer<sup>55</sup> has reported that in some trees (like *Pinus sylvestris* and various species of birch) starch deposits disappear during the winter months and are replaced by fats. In other trees (including the oaks, elms, etc.) this starch content is but slightly affected and very little fat formation is noted.

Despite the knowledge that this conversion takes place, only scattered pieces of work have been published on the chemistry of the fatty oils that occur in wood. The oil in the heart and sapwood of oak (species not given?) was shown by Metzger<sup>56</sup> to be a mixture of olein, palmitin and stearin. A semi-drying oil was extracted with ether from rasped basswood by Weichman.<sup>57</sup> The physical and chemical constants were determined but the chemical components of the oil were not completely identified. It is highly probable that many other woods contain appreciable amounts of fixed oils but this field remains unexplored since commercial quantities of such oils are usually found only in the fruits and seeds of the plant.

<sup>53</sup> Natl. Standard Dispensatory, 1916, p. 528.

<sup>54</sup> Czapek, Vol. I, p. 750.

<sup>55</sup> *Jahrb. wiss. Bot.*, 22, 73 (1890).

<sup>56</sup> Dissertation, Munich, 1896.

<sup>57</sup> *J. Soc. Chem. Ind.* (1895), 665; *Am. Chem. J.*, 17, 305 (1895).

### Organic Acids

Mention has already been made (Chapter 3) of the formation of formic and acetic acids, whenever finely divided wood is treated with aqueous  $H_2SO_4$ . The source of these acids is often a matter of conjecture. They may find their origin in the "lignin" of the wood, in the polysaccharides or in individual cases in the esters present in the oleo-resins. Schorger<sup>68</sup> has shown that in some woods these acids may be present in the free state. For example, *ginjo*, a Philippine wood (which corrodes metals) when extracted with cold water yielded 0.2 per cent of combined acetic and formic acids. In other cases free acids may have been formed by hydrolysis. Formic and acetic acids are frequently obtained when wood is steamed. Heuser<sup>69</sup> reports that liquors resulting from steaming of wood used in the production of brown mechanical pulp contained about 0.2 per cent acetic and 0.03 per cent formic acids, based on the weight of the wood used. Occasionally these same acids may be isolated from the aqueous distillates obtained when wood oils or oleo-resins are distilled with steam. Oil from the wood of *Gouphia tomentosa* Aubl. and steam distillates of *P. sabiniana* yield formic acid and the presence of acetic acid in many essential oils has been clearly demonstrated.

The occurrence in wood of higher homologs in the acetic acid series has seldom been clearly demonstrated although individual members of this series have been found among the products of wood distillation and individual essential oils (isolated from coniferous woods) have yielded isovaleric, caproic and capric acids.<sup>70</sup> Isovaleric, *n*-caproic, and lauric acids all appear to be present in the malodorous wood of *Gouphia tomentosa*.<sup>71</sup>

A substance widely distributed in plants is oxalic acid. The presence of calcium oxalate in various woods has been repeatedly indicated and crystals of this salt have been found in the wood of various oaks, hickory, walnut, and persimmon.<sup>72</sup> Many other woods also contain calcium oxalate. It has been suggested that the insolubility of calcium oxalate insures a means of removing excessive amounts of calcium from the cell sap and of preventing this calcium from functioning further in the metabolic processes of the plant.<sup>73</sup>

Jeffrey,<sup>74</sup> however, has pointed out that the calcium oxalate crystals

<sup>68</sup> *J. Ind. Eng. Chem.*, **9**, 561 (1917)

<sup>69</sup> *Papier-Ztg.*, **39**, 1280 (1914)

<sup>70</sup> Schorger, *Trans. Wiss. Acad. Sci. Arts and Letters*, **19**, Pt. II, 736; Gilde-meister and Hoffmann (Kremers), "Volatile Oils," I, p. 498.

<sup>71</sup> Dunstan and Henry, *J. Chem. Soc.*, **73**, 226 (1891)

<sup>72</sup> Record, "Economic Woods of the U. S.," p. 21

<sup>73</sup> Thatcher, "Chemistry of Plant Life," p. 127, Czapek, "Biochemie der Pflanzen," III, pp. 66-79.

<sup>74</sup> *Science*, **55**, 556 (1922).

are not formed by ordinary crystallization in the fluid of the cell sap<sup>6</sup> but by the action of living protoplasm under influence of the nucleus which is central to the crystal itself.

Czapek states that some of the inconclusive biochemical tests that have been used by biologists to indicate the presence of calcium oxalate crystals in plant tissues might apply equally as well to the calcium salts of other organic acids such as calcium malate or calcium citrate. Microscopic examination should be further substantiated by means of chemical analysis.

The technic of micro-identification often makes the recognition of malates in plant tissues a rather difficult matter. Tunmann<sup>66</sup> has suggested the use of a microsublimation method which depends on the formation of maleic acid crystals. Lenz<sup>67</sup> has reported the presence of calcium malate in the sap of the European birch and Warren<sup>68</sup> has shown that the "sugar sand" of maple sap (*Acer saccharum*) is composed largely of this salt. It is, therefore, highly probable that at times calcium malate will be found as an extraneous component of woody tissue. Similarly it is possible that calcium succinate may be present in certain woods. Goldschmidt<sup>69</sup> reported the presence of calcium succinate in the sap issuing from bark fissures of the white mulberry (*Morus alba* L.) and free succinic acid has been found in the wood oil of *Gouania tomentosa*. According to H. G. Smith,<sup>70</sup> basic aluminum succinate is deposited in the wood of the Australian *Orites excelsa* R. Br. of the Proteaceæ.

On the basis of the scattered evidence it is quite conceivable that the salts of other common organic acids may be occasionally extraneous components of woody tissue.

### Organic Nitrogen Compounds

The more recent analyses of wood indicate that the nitrogen content of wood is generally very low, usually well under 0.3 per cent.<sup>70</sup> A large part of this nitrogen is presumably due to the protein present in the dried protoplasm in the wood. These proteins have apparently received little or no study.<sup>71</sup>

In individual woods taken from trees characterized by their high alkaloidal content, an appreciable portion of the nitrogen may be due to the presence of pyridine, quinoline, or isoquinoline derivatives in the wood. Ordinarily such alkaloids are located in the leaves, bark, and in

<sup>66</sup> "Pflanzenmikrochemie," Berlin, 1913, p. 146.

<sup>67</sup> *Ber. Pharm. Ges.*, 19, 332 (1909).

<sup>68</sup> *J. Am. Chem. Soc.*, 33, 1205 (1911).

<sup>69</sup> *Sitzber. Wien. Akad.*, 85, II, 265 (1882).

<sup>70</sup> *Proc. Roy. Soc., New S. Wales*, 37, 107 (1903).

<sup>71</sup> Schroeder, *Tharandter Forstl Jahrbuch*, 24, 70, etc. (1874); Schwalbe's "Chemie der Cellulose," p. 439 (1918).

"Osborne, "Vegetable Proteins," p. 7 (1919).

the root, rather than in the wood, but a number of investigators have shown definitely that the xylem may contain these nitrogenous bases. This is true of the wood of berberin-yielding plants<sup>72</sup> and also of the wood of various species of *Cinchona* (from which quinine, cinchonidine, etc., are derived). In the case of the latter, the wood of the bole may contain as much as 0.25 per cent total alkaloids.<sup>73</sup> Even the older heart-wood may contain small but appreciable amounts of quinine.

The wood of several species of *Strychnos* also contains strychnine alkaloids. Strychnine and brucine are present to the extent of 0.96 per cent in the wood of *Strychnos colubrina* L. The wood of *Strychnos Nux-vomica* L. contains well over 2 per cent brucine.<sup>74</sup> Strychnine (but no brucine) was shown to be present in the wood of *S. Ticuté* Lesch. On the other hand, the wood of *Strychnos laurina*, Wall. contained no alkaloid whatsoever.<sup>75</sup>

A number of other tropical woods also contain poisonous alkaloids. The East Indian satinwood (*Chloroxylon Swietenia*) contains a crystalline substance, *chloroxylonine*,  $C_{22}H_{28}NO_7$ ,<sup>76</sup> m. 182-3°, which appears to be responsible for the dermatitis caused by the action of the sawdust of this wood.<sup>77</sup> The Central American *cocobolo* wood (*Dalbergia spp.*) used in the manufacture of knife handles in the U. S. also exhibits toxic properties that may be due to the presence of an alkaloid, the nature of which remains undetermined. Another alkaloid, also unidentified, is a component of the wood of an inferior type of Knysna boxwood or Kamassi wood grown in Southeast Africa. This substance is a heart depressant and resembles the curare-arrow poison in its action.

Occupational diseases due to the poisoning caused by these and other woods depend on the sensitiveness of certain individuals to the toxic substances in the wood. The suggestion has been made that only laborers immune to such poisons be selected for work in the industries utilizing cocobolo, satinwood, etc.

Derivatives of indol are also occasionally found in wood. As an example, both indole and skatole (its methyl derivative) are present in the wood ray parenchyma of *Celtis reticulosa* Miq.<sup>78</sup> The presence of the ill-smelling skatole<sup>79</sup> has also been reported in the wood of *Nectandra globosa* Mez.

<sup>72</sup> Czapek, Vol. III, p. 228.

<sup>73</sup> Howard, "Quinology of East India Plantations," p. 12 (1869).

<sup>74</sup> Greenish, cited by Czapek, Vol. III, p. 298.

<sup>75</sup> Boorsma, *Med. s' Lands, Plantentuin* (1900).

<sup>76</sup> Auld, *J. Chem. Soc.*, 95, 964 (1909).

<sup>77</sup> Garatt, *J. Forestry*, 20, 484 (1922).

<sup>78</sup> Herter, *J. Biol. Chem.*, 5, 489 (1909); Dunstan, *Proc. Roy. Soc. (London)*, 46, 211 (1889).

<sup>79</sup> Sack, *Pharm. Weekbl.*, 48, 310 (1911).

### Inorganic Components<sup>80</sup>

A residue of ash invariably remains after the complete combustion of any wood. In North American species that have been studied analytically, the ash content of wood usually varies between 0.2 and 0.9 per cent. Balsa wood (*Ochroma Lagopus* Sw.) of Central America, proves an exception with an ash content of approximately 2 per cent.<sup>81</sup> In a few instances European investigators have published the results of ash analysis that are considerably higher than this. Thus Nygard<sup>82</sup> reports 4.8 per cent ash in quassia wood; Becchi<sup>83</sup> reports 5.04 per cent ash in the dry sapwood of *Olea europaea* L., and Weber<sup>84</sup> reports over 2 per cent ash in the sapwood of larch (*Larix decidua* Mill.).

The general assumption might be made that the mineral content of heartwood is lower than that of sapwood. As early as 1834, Sprengel formulated this hypothesis and it has been borne out in certain cases since then. Other factors, however—such as the deposition of calcium salts in the heartwood—must be considered, and any sweeping generalizations regarding the ash content of heart and sapwood are of doubtful value.<sup>85</sup>

Frequently the ash content of wood in the branches and in the crown is higher than that of the trunk. Quite often, too, the average ash content of the total wood of an old tree is lower than that of a younger tree of the same species. For example, Weber<sup>86</sup> found in the stem of beechwood (*Fagus sylvatica* L.) an ash content of 0.56 per cent at the age of 10 years, 0.46 per cent at 20 years, 0.45 per cent at 40 years and 0.36 per cent at 50 years. Very similar results were obtained when oak woods of various ages were examined.

While the ash content of wood has been shown to increase or decrease seasonally in various species, a number of analyses show that these seasonal fluctuations are often too slight to warrant any general conclusions.

The principal metallic components in wood ashes are calcium, potassium, and magnesium. The common acid radicles are —CO<sub>3</sub>, —PO<sub>4</sub>, and —SiO<sub>3</sub>. Besides these, small amounts of sodium, manganese, aluminum, iron, sulfates and chlorides are almost invariably present in wood ashes.

Perhaps the most characteristic, although seldom the most abundant,

<sup>80</sup> An excellent, detailed discussion on the mineral substances in various woods is given by Czapek, "Biochemie der Pflanzen," Vol. II, pp. 400-414 (1920). Cf. also Wolff's "Aschenanalysen."

<sup>81</sup> Ritter and Fleck, *J Ind Eng Chem.*, 14, 1050 (1922).

<sup>82</sup> *Farm Notisbl.*, No. 9, 125 (1909).

<sup>83</sup> Cf. Wolff's "Aschenanalysen," 2, 103.

<sup>84</sup> "Allg Forst u. Jagdztg." (1873), p. 367.

<sup>85</sup> Cf. also Ritter and Fleck, *Ind. Eng. Chem.*, 15, 1055 (1923).

<sup>86</sup> Quoted by Czapek, Vol. II, p. 402.

component of wood ashes is  $K_2CO_3$ . The presence of this compound explains the value of wood ashes as fertilizer and as a raw material in the time-honored custom of making soft soap. The potassium content of wood ashes varies considerably. In rare instances the per cent  $K_2O$  drops to 5 per cent or even less. Quite frequently it ranges between 10 and 20 per cent and at times it reaches 40 per cent or more of the total ash content. As examples, the ash of a wood sample of *Abies pectinata* DC. contained 44.6 per cent  $K_2O$  and a sample of wood ashes from *Juglans nigra* L., contained 39 per cent  $K_2O$ .

In contrast to the potash content of wood ashes, the soda content is generally quite low and frequently ranges between 0.5 and 2.0 per cent. Here too, however, the outside extremes in soda content are very far from normal. Thus Wittstein in an early analysis of *Pinus montana* Mill. reports 24.46 per cent  $Na_2O$  in the ash, while Siewert reports only 0.04 per cent  $Na_2O$  in the wood of *Tectona grandis* L.<sup>87</sup>

In general, the lime content of wood ashes exceeds that of any other component. Wolff quotes a number of analyses on the ash of various hardwoods (including basswood, poplar, ash) in which the  $CaO$  content ranges between 60 and 78 per cent of the total ash content. The percentage of lime rarely drops below 20 per cent of the total ash, although in exceptional cases (e.g., a sample of *Abies pectinata* DC.) it has fallen to 10 per cent of the total mineral matter of the wood. In general, the lime content is considerably higher in the heartwood than in the sapwood, although here, too, exceptions occur. Molisch and others<sup>88</sup> have shown that in the heartwood of a number of hardwoods crystalline  $CaCO_3$  may be deposited in the true vessels, wood tracheids, wood fibers and in the parenchyma cells.

The magnesia content of wood ashes frequently lies between 5 and 10 per cent, although in exceptional cases (as in certain species of oak, and larch) it may exceed 20 per cent. Very low values (i.e., under 1 per cent) are quite rare. As usual, it is difficult to generalize regarding the correlation between  $MgO$  content and the age of the wood. In the case of a species of beech (*Fagus sylvatica* L.) the  $MgO$  content increases gradually with the age of the tree. At the age of 10 years the  $MgO$  content in the ash was 12.4 per cent. At 220 years it had increased to 19.5 per cent. On the other hand, cases may be cited in which  $MgO$  content falls as the age of the wood increases. This was shown in a species of oak (*Quercus pedunculata* Ehrb.) the ash of which—at 15 years—contained 13.4 per cent  $MgO$ . At the age of 345 years, the  $MgO$  content of the oak ash had dropped to 2.35 per cent.

The iron content ( $Fe_2O_3$ ) of wood ashes is frequently under 1 per

<sup>87</sup> Czapek, Vol. II, p. 405

<sup>88</sup> *Sitzber. Wiens. Ak.*, **80**, Pt. 1, 82 (1879), *et al.*

cent. However, it often reaches 2-3 per cent and may, in individual cases, exceed these figures. In a rare case, that of a spruce wood sample, 10 per cent of the total ash content consisted of ferric oxide.

Usually the  $Mn_2O_4$  and  $Al_2O_3$  contents of wood are quite low, often under 1 per cent, seldom ranging above 10 per cent of the total ash. A striking exception to this general rule is shown in the case of an Australian wood (cited in a previous section) which contains aluminum succinate and the ash of which contains well over 75 per cent  $Al_2O_3$ . Other woods also form exceptions to the rule of low  $Mn_2O_4$  content. Thus a sample of wood of *Abies pectinata* DC. (analyzed by Schroeder), yielded an ash containing 40 per cent of  $Mn_2O_4$ .

In a few cases other metallic substances have been found in wood. Forchhammer<sup>89</sup> reported the presence of nickel and cobalt in samples of oakwood, and Frankforter<sup>90</sup> has made the surprising discovery of particles of metallic copper in the wood of an individual oak tree in Minnesota which was possibly killed by absorption of copper salts from the soil.

Phosphates are invariably present in wood ashes. The  $P_2O_5$  content of the ash is subject to very wide variations, ranging from less than 2 per cent to about 30 per cent. Thoms<sup>91</sup> cites the interesting example of teakwood in which calcium phosphate concretions occurred in the xylem and the ash of which contained over 29 per cent  $P_2O_5$ .

Chlorides are often components of wood ashes in traces only. The amounts seldom rise above 3 per cent of the total ash. In individual cases, however, higher amounts are found as in the case of a sample of horse-chestnut wood, the ash of which contained over 6 per cent Cl.

Woody tissue is usually low in sulfates (calculated as  $SO_4$ ) and this content seldom rises above 5 per cent of the total ash. Here, as in all other cases, however, individual exceptions occur. Thus the ash of a sample of white pine (*Pinus Strobus*) contained over 10 per cent of  $SO_4$ .

Silicates are invariably present in wood ashes. Often the amounts range between 1 and 3 per cent of the total ash but frequently, too, rise far above these figures. The ash of Norway spruce wood is always high in silicates. Czapek cites the case of a sample of *Picea excelsa* Link., the ash of which contained over 36 per cent  $SiO_2$ .

While most of the mineral components of wood may be considered extraneous substances, recent investigations indicate that the silica or silicates may be in part integral components of the cell wall. Brown<sup>92</sup> reports that the fibers and tracheids of all woods examined by him actually contained a siliceous skeleton, largely insoluble in such mineral acids as

<sup>89</sup> Cited by Czapek, "Biochemie der Pflanzen," II, p. 410. (Reference incorrectly given.)

<sup>90</sup> *Chem. News*, 79, 44 (1899).

<sup>91</sup> *Landw. Versuchstat.*, 23, 413 (1879).

<sup>92</sup> *Bull. Torrey Botanical Club*, 47, 407 (1920).

HCl and HNO<sub>3</sub> but disappearing on treatment with hydrofluoric acid. The skeleton seems to consist of miniature rods and in the case of *Tecoma* wood the number of these rods was estimated as 100-200 per fiber.

The presence of these "silicious rods" may have an important bearing on the mechanical properties of wood and may explain the fact that when water-saturated wood dries, it shrinks very slightly in length. An interesting feature is that the silicon content of the woods which are reinforced by Brown's "silicious rods" is only a fraction of 1 per cent of the weight of the organic matter in the xylem.

# PART III

## PROXIMATE AND SUMMATIVE ANALYSES OF WOOD

### Chapter I

#### Introduction

##### Ultimate Analyses of Wood

During the earlier part of the 19th Century, concomitant with the classical researches of Payen, the analysis of wood often consisted in the determination of its elementary composition, with the practical end in view of gauging its fuel value. Ultimate analytical data of this type threw little or no light on the chemistry of the woody tissue, in fact they served to obscure in part the results of Payen's brilliant work.

Analysis by six or seven early investigators (that have been compiled in Table XI) yielded surprisingly concordant results in which the extreme values for carbon and hydrogen varied very little from the approximate mean values of 50 per cent carbon and 6.0 per cent hydrogen. Largely as a result of the work of Thenard and Gay-Lussac, the thought persisted that carefully purified *wood*, no matter from what source, consisted of one individual chemical substance.

TABLE XI  
ELEMENTARY COMPOSITION OF WOOD

Investigators	Reference	Per Cent C (Approx.)	Per Cent H (Approx.)	Per Cent N	Per Cent Ash
Thenard Gay-Lussac	Quoted in <i>Compt rend.</i> , 8, 51 (1839).	53.0	5.2 (Expressed as 47% H <sub>2</sub> O)	—	—
Petersen and Schödler	<i>Ann. Chem. Pharm.</i> , 17, 139 (1836)	48.2— 50.2	5.35—6.9	—	—
Payen	<i>Compt rend.</i> , 8, 170 (1839)	49.3— 52.9	6.0—6.2	—	—
Chevandrier	<i>Ann. Chim. phys.</i> [3], 10, 143 (1844).	49.9— 51.8	6.07—6.32	1.0—1.3	.78—3.67
Gottlieb	<i>J. prakt. Chem.</i> [2], 28, 385 (1883).	48.9— 50.4	5.9—6.3	.04—.10	.28—.57

### Proximate Analysis

The gradual development of analytical procedures used in the study of wood requires little comment at this point. It has been outlined in sufficient detail in a previous chapter (Chapter 3, Part II of this monograph). Payen<sup>1</sup> blazed the trail by demonstrating that *cellulose* was a regular component of all woody tissues and that other substances (grouped together under the collective name of "lignin") were also present. Most modern analytical procedures take into account these two components of the cell wall as well as a number of other extraneous substances which fall into the general class of extractives. Consequently, the ultimate analysis of wood has been entirely displaced by proximate analytical procedures which give a somewhat clearer insight into the nature of the components and the groups or linkages present in wood.

It should not be imagined, however, that such analytical schemes are entirely satisfactory. At best they yield results that are meagre enough and leave much to be desired. From what has been said in preceding chapters regarding the lack of definition of the terms cellulose and lignin and the difficulty in judging which substances are extraneous and which are an integral part of the cell wall, it is obvious that any procedure for the analysis of wood must be a purely arbitrary one. For example, if we standardize one method for the isolation and determination of cellulose, we may expect reproducible or comparable results by the use of this method; but these results may be quite different from those obtained by means of another, equally well standardized procedure. Much depends on the definition of the term "cellulose" that has been accepted by the individual analyst. At present we have few criteria for judging which method gives the best index of the *true cellulose content* of any wood. "Cellulose" remains an elusive term. We can simply judge which method is the most convenient one, or the one most easily adapted to our purpose. The same is true, perhaps to a lesser degree, of some of the methods devised for determining other components of wood.

In the United States two types of proximate analyses of wood have been developed: (1) the analytical methods of Schorger and his successors at the Forest Products Laboratory<sup>2</sup> and (2) the summative methods of analysis proposed by Dore at the University of California.<sup>3</sup>

Schorger realized that while the solubility of wood in different reagents or solvents did not actually furnish a means of determining individual components, it nevertheless indicated the types of extraneous

<sup>1</sup> Compt. rend., 7, 1052, etc.

<sup>2</sup> J. Ind. Eng. Chem., 9, 556, 561, 624, and 748 (1917); 14, 933 and 1050 (1922), etc.

<sup>3</sup> J. Ind. Eng. Chem., 11, 556 (1919); 12, 472, 476, and 984 (1920).

substances present and gave some useful data on the chemical properties of the individual wood. His scheme included the percentage solubility of the wood in cold water, in hot water, in ether, and in 1 per cent NaOH solution. The water soluble material consisted largely of tannins and carbohydrates. Ether extracted mainly fatty substances and resins. The alkali soluble material was not very clearly defined. It consisted of a part of the so-called "lignin," pentosans, and other carbohydrates and any acid substances generally that were in the wood. Schorger's other determinations included cellulose, ash, pentosans and methylpentosans, as well as the percentage of "methoxyl" and the acetic acid generated by treatment of the wood with dilute sulfuric acid. Originally Schorger's method did not include a "lignin" determination, but this determination has since been added by the Forest Products Laboratory.

Results obtained by Schorger's method "overlap" and in no case does the sum of all individual determinations even approximate 100 per cent. Details of Schorger's methods of analysis are reserved for subsequent chapters.

Dore's scheme for the analysis of wood differs from that of Schorger in that it aims at a *summative* analysis. In other words, the sum total of all of Dore's determinations approaches 100 per cent and he deliberately seeks to avoid overlapping of results. Originally Dore effected a separation of wood substance into the following fractions, which represent the results of successive operations (1) loss on drying, (2) fraction soluble in benzene, (3) fraction (from 2) soluble in alcohol, (4) fraction (from 3) soluble in water, and (5) fraction (from 4) soluble in 1 per cent NaOH. In this completely extracted material, cellulose and lignin were then determined.

Subsequent investigations, however, showed Dore certain weaknesses in his original scheme. Apparently the digestion with 1 per cent alkali served to diminish the yields of cellulose and lignin. This was not due to a greater degree of "purification" of these fractions, but to an actual destruction of the material. Besides this, the water soluble and alkali soluble fractions possessed a very vague significance and the numerical expression of these fractions contributed little of real value as an analytical expression of what components were present in wood. Other flaws in Dore's original scheme led him to adopt the following methods which gave satisfactory results in the case of *coniferous* woods: (1) loss on drying at 100° C. followed by (2) a benzol extraction followed by (3) a 95 per cent alcoholic extraction of the residue. Cellulose, lignin, and *soluble* pentosans were then determined on the extracted wood and mannans and galactans were determined on samples of the original wood. Details of these determinations will be given at appropriate places in future chapters. Using this analytical scheme on redwood (*Sequoia*

*sempervirens*), yellow pine (*Pinus ponderosa*) and sugar pine (*P. lambertiana*), Dore obtained results which accounted for 101.5 to 102.5 per cent of the wood. This summation is entirely satisfactory when we consider the limitations of the methods employed.

Dore later explored his various fractions by studying the distribution of such groups as the furfural-yielding groups, acetic acid-yielding groups, and methoxyl groups over the lignin and cellulose of red-wood. His results showed that about half of the furfural emanated from the cellulose fraction and very little (less than 5 per cent) from the lignin fraction. The acetic acid-yielding material was associated almost entirely with the cellulose fraction, while the methoxyl content was due almost totally to the lignin. This is in harmony with other experimental data that have been discussed in previous chapters and again indicates the lack of homogeneity in the so-called cellulose fraction.

Dore's summative scheme of analysis as outlined required modification before it could be applied satisfactorily to hardwoods. In a study of *Quercus agrifolia*, Dore found, after extracting the dried wood successively with benzol and alcohol, that a cold water extraction, followed by an extraction with 5 per cent sodium hydroxide solution, was required before the cellulose, lignin, and "residual mannans and galactans" could be satisfactorily determined. Pentosans (which had not been removed by the alkali extraction) remained largely in the cellulose fraction. When the small amounts of pentosans "not otherwise accounted for" had been determined in the filtrates from the cellulose fraction and added to the sum total of cellulose, lignin, mannans, galactans and extractives, Dore's results on oak wood totalled 100.5 per cent. In this case the alkali digestion had entirely removed the acetic acid-yielding groups and had eliminated a good share of the pentosans. The methoxyl groups, as usual, remained largely with the lignin.

A European proximate method of analysis, quite similar to that of Schorger, has been used by Schwalbe and Becker.<sup>4</sup> They determined successively ether and alcohol soluble extractives on individual samples of wood. The sum of these two determinations usually checked rather closely with the "alcohol-benzol soluble" material determined on a separate sample of the same species. They also determined cellulose, lignin, ash, nitrogen (calculated as protein), pentosans, "methylpentosans" and "pectins." The value of the two latter determinations is highly questionable, as we have shown previously.<sup>5</sup> Schwalbe and Becker adopted Schorger's acid hydrolysis method and also determined the per cent of CH<sub>3</sub> in wood (methyl number). They gave values for cellulose cor-

<sup>4</sup> Z. angew. Chem., 32, 229-31 (1919).

<sup>5</sup> Cf. Part II, Chapter 2.

rected for pentosans in cellulose. In general their data are fairly comparable with those obtained by the U. S. Forest Products Laboratory.

A different type of *summative* analysis from that used by Dore was devised by Konig and Becker.<sup>6</sup> Their "summation" of the components of wood included lignin, ash, resins, proteins, hemicelluloses (i.e. hexosans and the more readily hydrolyzable pentosans), "insoluble pentosans" (remaining after hydrolysis with dilute acid under pressure) and "ortho cellulose" (obtained not by direct determination but by subtracting the sum of the other components from 100). The extremely arbitrary methods used in determining hemicelluloses makes the figures for cellulose very uncertain, especially as a different "hemicellulose procedure" is recommended for every species of wood studied.

For the present it is unnecessary to discuss further the general types of proximate wood analysis. We cannot leave the subject, however, without emphasizing what appears axiomatic to us in interpreting analytical data. The results obtained with any one scheme of proximate analysis should not be considered comparable with those given by another scheme of proximate analysis. Schoiger's data would not be comparable with those obtained by Dore. In individual cases results obtained by various methods of analysis *may* be in fairly close agreement with each other but this may be entirely fortuitous and cannot be generally expected.

There is another point which we feel should be stressed. Proximate analytical data taken *per se* throw no light on the *chemical* constitution of the various substances as they occur in the wood. The reagents used in the analytical study of a heterogeneous material like wood, undoubtedly cause chemical changes in some of the components of the wood and they never yield cellulose or lignin fractions that can be considered "pure" chemical entities which occur in the original wood. It is, therefore, dangerous to allow an analytical procedure to become a fetish and to attempt to make analytical data the basis for speculations on the constitution of wood constituents. This seems an elementary precaution and quite an obvious one to the writers and yet just such distortions of analytical data have been made in the past.

<sup>6</sup> *Z. angew. Chem.*, 32, 155 (1919); for details cf. *Papierfabrikant*, 17, 982-7, 1014-19, 1171-1174 (1919).

## Chapter 2

# The Sampling of Wood; Miscellaneous Determinations

### Sampling

Three points must be considered in obtaining representative wood samples for analysis: (1) the portion of the tree from which the wood is taken, (2) the uniformity of the sample, and (3) the optimum size of the wood particles in the sample chosen for analysis.

The importance of the first factor must be obvious in the light of previous discussions of the variations in the extraneous components of wood. Differences in the cellulose and lignin content of heartwood and of sapwood in the same species when a standardized procedure has been used<sup>1</sup> serve to emphasize this same point. Johnsen has also given analytical data which show differences in the cellulose contents of the same species when wood samples are taken from thebole of the tree at different heights from the ground.<sup>2</sup> Similarly the work of Klason on lignin makes it apparent that wide variations in the lignin content of wood in the same tree may occur even when a definite analytical procedure is followed. The gnarled wood (known as "Rotholz" or "Kjurig ved" in Sweden) showed a lignin content of approximately 37 per cent, while the wood of the same branch, taken at a different point showed a normal lignin content of about 28 per cent.<sup>3</sup>

Schorger, in his first paper on the analysis of wood, outlined his methods for obtaining wood samples. Strength tests at the Forest Products Laboratory showed that some twenty feet from the ground, the wood of the tree was most uniform and a cross-sectional disc, about two inches in thickness was taken at this point. From this disc, the analyst split out two, diagonally opposite sectors, the size of which varied with the size of the tree trunk. Schorger used his wood samples in two forms—sawdust and shavings (not exceeding 0.005 inch in thickness). Shavings obtained with a plane were passed through a shredding grinder, and the material was then screened. The material which passed a 40-mesh sieve was rejected and that remaining on the screen was uni-

<sup>1</sup> Ritter and Fleck, *Ind Eng. Chem.*, 15, 1055 (1923).

<sup>2</sup> *Paper*, 20, No. 8, 15 (1917).

<sup>3</sup> *Cellulosechemie*, 4, 83 (1923).

formly mixed. The samples were always kept in sealed containers. Johnsen and Hovey<sup>4</sup> used wood rasps in preparing their wood samples and they worked with raspings passing an 80 mesh, but retained on a 100 mesh sieve. A number of other investigators (notably Dore) have also discussed the sampling of wood but in general they gave no definite information regarding the size of particles best suited to their purpose.

Large or non-uniform wood particles made it difficult to remove lignin from cellulose. Dore<sup>5</sup> showed that in the cellulose determinations made on redwood "shavings" from 0.77 to 5.78 per cent lignin was retained in the cellulose fractions. Under similar conditions, cellulose from coarse sawdust retained 0.16 to 1.64 per cent lignin, while that isolated from fine sawdust seldom retained more than 0.5 per cent lignin. Fine sawdust was therefore recommended by Dore, but he points out the danger of obtaining unrepresentative samples by using fine screens. In general (according to Dore), heavily lignified tissues resist mechanical disintegration more than do the less lignified tissues of the springwood and a larger proportion of lignin might be expected in the coarser fractions. In the light of recent studies by Ritter<sup>6</sup> it is highly probable that springwood actually contains *more* lignin than does summerwood. This is due to the fact that for a definite weight of springwood Ritter claims a higher percentage of "middle lamella lignin" than for the same weight of summerwood. On the other hand, Dore's general conclusions might well be correct if we amended them to read that the *coarser particles contain a higher proportion of summerwood*. This resistance would be due, however, not to the lignin content but to the resistance of the denser wood to mechanical disintegration. The springwood may contain less lignin in the secondary layer (i.e., the cell wall other than the middle lamella) than does the summerwood, even though the total lignin content of springwood is higher. This possibility, coupled with the fineness of division of the springwood particles might account for the greater retention of lignin by some of the coarser particles of redwood sawdust, after chlorination.

The work on sampling by Schorger was extended by Mahood,<sup>7</sup> who examined the effect of the size of wood particles on the yield of cellulose obtained. Material which passed an 80 mesh sieve, but which was retained on a 100 mesh sieve gave the best cellulose yields. Mahood also showed that by using a combination of sawing and grinding (i.e., ground sawdust) he was able to obtain a sufficiently large and representative sample of the wood in this 80-100 mesh fraction to warrant its use.

<sup>4</sup> *Paper*, 21, No. 23, 40 (1918).

<sup>5</sup> *J. Ind. Eng. Chem.*, 11, 556 (1919).

<sup>6</sup> *Ind. Eng. Chem.*, 17, 1194 (1925).

<sup>7</sup> *J. Ind. Eng. Chem.*, 12, 873 (1920).

in Schorger's analytical scheme. Wood particles in this state of subdivision were readily attacked by the reagents and could be easily manipulated. In some later work, Mahood and Cable<sup>8</sup> reached similar conclusions regarding the size of wood particles, and Mahood's suggestions on sampling have therefore been generally adopted by the Forest Products Laboratory.

### Determination of Water

When conifers of low resin content or when hardwoods are to be analyzed, the moisture determination may be made by drying a (2-3 gram) sample to constant weight at 100° C., or by drying for 6-7 hours in an air oven at 105° C. Since dry wood is exceedingly hydroscopic, weighings should always be made in weighing bottles with ground-in glass stoppers. Schorger<sup>9</sup> has shown that drying wood in an air oven at 105°-107° is more effective than drying in a vacuum desiccator over fresh concentrated H<sub>2</sub>SO<sub>4</sub> at 30-60 mm. pressure and 55-60° C.

More rapid drying may be attained by the use of a Gaede vacuum pump at a temperature of 90° C.<sup>10</sup> but in general the simpler expedient of drying at atmospheric pressure is to be recommended. Cellulose appears to hold water with extreme tenacity and cannot be dried by the use of some of the more common substances used in dehydration.<sup>11</sup>

If the wood sample contains very much resin, a part of this substance will be lost gradually on drying and unless special precautions are taken, the moisture determination may give high results. Usually, however, this loss manifests itself only after 10-15 hours of drying. Schorger showed that a sample of longleaf pine containing 9 per cent resin, lost 4.84 per cent of its weight when dried at 105-107° for 3 hours, and that there was no further change in weight until the sample had been heated well over 11 hours. At the end of 21 hours, the loss was only 5.05 per cent and from then on, the sample lost very gradually, until after 711 hours the total loss in weight was only 6.35 per cent, indicating that not more than a 1.41 per cent loss had been incurred during the final 708 hours. In the case of a basswood sample, the change in weight after the first 3 hours was very slight and only 0.5 per cent of the weight of the sample was lost during 700 hours of heating.

When essential oils or other volatile substances are present, the water content of wood may be determined by placing 25 grams of the finely powdered sample in a 250 cc Erlenmeyer flask together with 75 cc of water-saturated xylol. On heating, the water distils over with the xylol,

<sup>8</sup> *J. Ind. Eng. Chem.*, **14**, 933 (1922).

<sup>9</sup> *J. Ind. Eng. Chem.*, **9**, 561 (1917).

<sup>10</sup> Gaefke, Dissertation, Dresden, 1919.

<sup>11</sup> Jentgen, *Z. angew. Chem.*, **33**, 1544 (1910).

and the distillate may be collected quantitatively in a graduated tube provided with a funnel- or pear-shaped mouth. The amount of water may then be read off directly, since the essential oil is soluble in the hydrocarbon.<sup>12</sup>

Ordinarily all subsequent analyses of wood are made on air-dried samples, in which the moisture content has been accurately determined. Results are then calculated to the oven dry basis.

### Determination of Volatile Oils

In rare instances, it is desirable to determine the volatile oil content of wood. Schorger suggests the following procedure: The moisture in wood is determined by the xylol method. Ten grams of sawdust are then weighed into an accurately weighed, wide-mouth Frlemeyer flask, provided with a glass stopper. The glass stopper is then replaced by a 2-hole rubber stopper which is entered by two tubes, the one extending nearly to the bottom of the flask and serving as steam inlet, and the other acting as an outlet tube for connection with a condenser. The flask is heated in an oil bath, maintained at 110° C., and steam is passed in gradually until all of the oil has distilled over. The rubber stopper is then withdrawn from the flask, into which are washed any particles of sawdust adhering to the tubes, stopper, etc. The heating of the flask in the oil bath is then continued until nearly all the water has been expelled. Evaporation may be expedited by applying suction to the flask, which is then wiped clean and dried to constant weight, the original glass stopper being used to seal the flask. The weight of dry wood substance is found in this way. The difference between this weight and the weight of the original samples = water plus volatile oil. The amount of volatile oil is found by subtracting from this figure the amount of water found by the xylol method.

Schorger showed that by deducting water (obtained by the xylol distillation) from the total loss in weight obtained by drying at 105-107° C. figures for essential oil were obtained that were appreciably lower than when the oil was expelled by steam. The method outlined above is, therefore, assumed to give results which are more nearly correct. If, however, a wood contains or gives rise to considerable amounts of other components (like formic and acetic acids) which are volatile with steam, it is quite probable that either method would yield high results.

### The "Acid Hydrolysis" Determination

Schorger has devised a standardized procedure for the determination of volatile acids that are formed when wood is heated with aqueous sulfuric acid. The method is as follows:

<sup>12</sup> Schorger, *loc. cit.*; Forest Service Circular No. 134

"Approximately 2 g. of sawdust are placed in a 250 cc Erlenmeyer flask and 100 cc of 2.5 per cent  $H_2SO_4$  added. The flask is connected with a reflux condenser and the contents are boiled gently for 3 hours and then allowed to cool. The interior of the condenser is washed down with a little distilled water and the contents of the flask are transferred to a 250 cc graduated flask. Distilled water free from carbon dioxide is added to make up to the mark and the solution allowed to stand several hours with frequent shaking, and then filtered.

"A wide-mouthed, round-bottomed, 750 cc flask is provided with a rubber stopper containing: (1) a dropping funnel; (2) a glass tube drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; and (3) a Soxhlet connecting bulb-tube. An ordinary condenser is used, to the end of which is attached (as receiver) a 500 cc distilling flask cooled with a stream of water and connected with a manometer and suction pump.

"A few pieces of pumice are placed in the 750 cc flask, to which are added 200 cc of the filtrate obtained above (in the case of hardwoods use 100 cc). The flask is heated in an oil bath maintained at 85° C, while the pressure is reduced to 40 to 50 mm. When the volume of the contents of the flask is reduced to about 20 cc, distilled water is added through the dropping funnel, drop by drop, at the rate at which distillation actually takes place. When 100 cc of wash water have been distilled over, the distillate is titrated with N/10 NaOH using phenolphthalein as indicator. If (a) 200 cc or (b) 100 cc of solution were taken for distillation, the number of cc of NaOH used is multiplied by (a) 5/4, or (b) 5/2, respectively, and calculated as acetic acid.

"All the distilled water used in this determination should have been recently boiled to expel carbon dioxide."

Formic acid may be present among the volatile acids as well as acetic acid and other organic acids are not excluded. Some investigators ascribe the acetic acid entirely to acetyl groups in the lignin, but, as we have stated in a previous chapter, this is not necessarily the source and probably not the only source of the acid. The "acid hydrolysis" would include any free volatile acids originally present in the wood. It would also include volatile acids resulting from the partial hydrolysis of esters in the resins. Furthermore, the standardized acid hydrolysis causes a marked decomposition of the wood substance and a part of the volatile acids may be formed in this way.

Experimental data have shown that certain woods yield free volatile acids without the use of  $H_2SO_4$ , simply by treatment with cold water. Some woods are known to lose as much as one-third of their original weight under the conditions of Schorger's acid hydrolysis. With increasing strength of acid, individual woods give increasing yields of acetic

acid. This was shown by Schorger in the case of yellow birch. Two and one-half per cent of sulphuric acid (according to the standardized procedure) yielded 3.99 per cent acetic acid; 5 per cent  $H_2SO_4$  gave 4.31 per cent acetic acid, and 10 per cent  $H_2SO_4$  yielded 4.53 per cent of volatile acids. It is impossible then to place our finger on all the components of wood that serve as precursors of acetic acid.

### Determination of Nitrogen

This determination is seldom made in American practice. Nitrogen in wood may be determined by treating 0.7 gram of sample by Gunning's modification of the Kjeldahl method. The results may be arbitrarily calculated as protein by multiplying the per cent nitrogen by 6.25.<sup>13</sup>

### Determination of Ash<sup>14</sup>

Mineral matter in wood may be determined by incinerating a representative sample in a shallow platinum dish in a muffle furnace at dull red heat. It is well to stir the contents of the dish from time to time so as to insure complete combustion.

After the ash has been weighed a test may be made for unburnt carbon by treating the mineral residue with dilute HCl. If the combustion is incomplete, carbon will appear as black suspended matter. Schwalbe and Sieber<sup>15</sup> suggest the use of small amounts of ammonium nitrate or 3 per cent  $H_2O_2$  to oxidize tenaciously retained carbon.

The ash may be analyzed further for its various mineral components. The occurrence of these substances in wood ashes has been fully discussed in a previous chapter.

### Determination of Fractions Dissolved by Various Solvents (Extractives)

The *ether soluble material* in wood represents largely fats, resins, and oils, and may be determined by extracting 3-4 grams of the finely divided wood with ether in a Soxhlet extractor for 4-5 hours, and by weighing the residue after evaporation of the solvent.<sup>16</sup> Schorger also attempted to make this determination by noting the loss in the weight of wood extracted but this method did not yield reliable results.

Waxes have been included among the ether soluble extractives but we still lack reliable experimental data to show the presence of true waxes in wood.

In general, coniferous woods yield a much higher percentage of ether

<sup>13</sup> Dore and Miller, *Univ. California Publications in Zoology*, **22**, No. 7, 388 (1923); Schwalbe and Becker, *Z. angew. Chem.*, **32**, I, 229 (1919).

<sup>14</sup> Schorger, *loc. cit.*

<sup>15</sup> "Betriebskontrolle"

<sup>16</sup> Schorger, *loc. cit.*

soluble substances than do the hardwoods although there are noteworthy exceptions to this rule. Basswood, which contains a semi-drying oil, averages nearly 2 per cent of ether soluble extractives, while western larch averages well under 1 per cent of ether-soluble material.

*Alkali soluble substances in wood* are determined according to Schorger by treating 2 grams of the original sawdust with 100 cc of 1 per cent NaOH in a 250 cc beaker. The beaker is covered with a watch glass and placed in a pan of boiling water (maintained at constant level) for exactly one hour. The contents of the beaker are stirred occasionally during the extraction. The material is then collected on a weighed alundum crucible, washed thoroughly with distilled water, then with aqueous acetic acid and again with water, after which the crucible is dried and weighed and the loss in weight calculated.

Since alkali has no specific action on wood, and attacks a number of different components, the significance of the determination is not very clear. Dilute sodium hydroxide solutions remove a part of the lignin and pentosans and a part of the hexosans, as well as the free acids present in the resins. Alkali treatment probably also causes a partial hydrolysis of esters present in the wood. The hardwoods, which contain a much higher proportion of pentosans than do the conifers, are usually attacked more rigorously by alkali than are the softwoods. It would be misleading, however, to make the statement that the content of alkali soluble material of *angiosperms* is *always* higher than that of the *gymnosperms*. Individual samples of Western yellow pine and longleaf pine run higher in alkali soluble substances than do certain samples of shellbark hickory or sugar maple.

The total *hot water soluble material* and also the total *cold water soluble material* in wood were determined by Schorger. The chief substances extracted from wood by means of water are the tannins, alkaloids, and some of the simpler carbohydrates. Certain polysaccharides (*e.g.* galactans) are also removed in colloidal solution. Heating with water may also cause the partial hydrolysis of some constituent groups in lignin or in the resins and so we may expect free organic acids and methanol in the aqueous extract. In individual dyewoods, water may also dissolve the precursors of dyestuffs.

The hot water-soluble substances were determined by heating two grams of finely divided wood with 100 cc of distilled water in a 300 cc Erlenmeyer flask provided with a reflux condenser. After the water had been boiled gently for 3 hours the contents of the flask were transferred to a weighed alundum crucible, washed with hot water, dried and weighed. The loss in weight was due to the material extracted with hot water. Cold water soluble substances are determined by extracting 2 grams of the wood for 48 hours with 300 cc of water at room temperature. The

mixture should be stirred at frequent intervals. The analysis is completed as in the case of the hot water soluble determination.

The percentage of cold water extractives is always lower than that of the hot water soluble substances in the same sample. Here again the determinations cannot be easily correlated with definite components in the wood, and are chiefly valuable in indicating whether a high tannin content may be expected.

### Extraction Methods Used in Summative Analysis

The extraction methods applied by Dore<sup>17</sup> have been mentioned in the preceding chapters. In determining the *benzene soluble material*, Dore places 2 grams of the *oven dried* sample in an alundum thimble and subjects it to extraction with benzene for 6 hours in a Soxhlet apparatus. The solvent is then evaporated and the residual extract dried for 1 hour at 100° C. and weighed. The wood residue in the thimble is then extracted further with 95 per cent alcohol for 6 hours. The solvent is subsequently evaporated and the residue dried and weighed as before. This weight is termed the *alcohol extract*. Various of Dore's determinations (cellulose, lignin, etc.) were made on *coniferous* wood samples previously extracted by the above methods.

In the case of hardwoods, Dore also determines the cold water soluble material (in wood samples already subjected to the benzene and alcohol extractions) by a method similar to that described by Schorger (except that 200 cc of water are used and the extraction period is limited to 24 hours). The wood residue from this extraction is then transferred to a beaker and treated with 100 cc of 5 per cent NaOH for 24 hours. It is then filtered off on the same crucible used in the cold water determination and washed successively with water, dilute acetic acid and again with water. The loss in weight from the previous weighing (i.e. from the wood residue insoluble in cold water) represents the material soluble in 5 per cent NaOH. The determinations of other components in the hardwoods were made on *completely extracted* wood samples.

<sup>17</sup> Loc. cit.

## Chapter 3

### The Determination of Cellulose

#### The Method of Cross and Bevan

In the chapter on cellulose, we stated that in the United States the term *cellulose* (when used by analytical chemists) generally referred to a residue remaining after wood had been delignified by the use of a chlorination method. The quantitative procedure for the isolation of cellulose was devised by Cross and Bevan<sup>1</sup> who subjected the dried material to treatment with 1 per cent NaOH solution, and then treated the filtered and washed residue with a slow stream of moist chlorine gas. A lively reaction ensued, in which the lignin was chlorinated and this "lignone chloride" was then dissolved away from the cellulose (after washing with water) by treating the material with a hot 2 per cent solution of Na<sub>2</sub>SO<sub>3</sub> to which a small amount of dilute NaOH solution had been added. The residual cellulose was "thrown upon a cloth filter and washed with hot water," and if necessary bleached white with 0.1 per cent sodium hypochlorite or potassium permanganate, followed by successive washings with sulfuric acid and water. The residue was then dried and weighed. Cross and Bevan state that "cellulose examinations by this method give what may be considered the maximum yield." A few of the earlier results obtained by these investigators (and recalculated from their figures—"Cellulose," p. 195) are of interest, since they are not strikingly different from data obtained by later investigators who modified the Cross and Bevan procedure. Samples of pine, beech, sycamore, and birch yielded respectively 64.1, 53.3, 58.8, and 63.4 per cent cellulose.<sup>2</sup>

The reagents used by Cross and Bevan in removing encrusting material have been retained by most American chemists and by a number of European investigators. However, the original method has been subjected to revision and modification from time to time and it is probably still undergoing an evolution. Taken by and large, it is the most satisfactory procedure that we have for determining cellulose in wood.

<sup>1</sup> "Cellulose," pp. 95, 195

<sup>2</sup> Compare these figures with those given in the final chapter of Part III of this monograph.

### Modifications of the Cross and Bevan Method

Important modifications of the method were instituted by Renker<sup>3</sup> who worked with moistened material and used a stream of cold chlorine. Renker also preferred to eliminate the pretreatment of wood with 1 per cent NaOH and extracted his original material with alcohol-benzol mixtures. The cellulose residue, obtained after chlorination, he treated immediately with sulfurous acid so as to prevent oxidation.

Renker's modified procedure was adopted by Schorger in his analysis of wood.<sup>4</sup> Two grams of wood shavings were extracted during 3-4 hours with a mixture of equal parts of benzol and alcohol. After the solvent had been evaporated, the shavings were thoroughly washed with hot water, using a suction pump. The moist shavings were then trans-

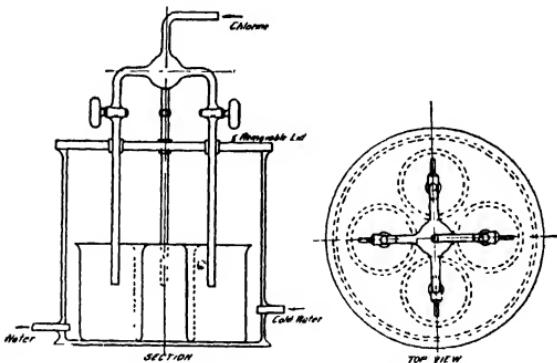


FIG. 6--Chlorination Apparatus used by Schorger.

ferred with a pointed glass rod to a 250 cc beaker, evenly distributed over the bottom and subjected to a stream (at the rate of 40 bubbles per minute for each sample) of washed chlorine gas, for half an hour. The chlorination was carried out in a specially designed apparatus of the type shown in Figure 6. This permitted the analyst to make four cellulose determinations simultaneously.

The end of the tube delivering chlorine gas was kept about  $\frac{1}{2}$  inch above the shavings and at intervals of 6-7 minutes the material was stirred and the positions of the beakers were changed. The heat of reaction was controlled and a low temperature maintained during chlorination by the use of running water as shown in the figure.<sup>5</sup>

<sup>3</sup> "Bestimmungs methoden der Cellulose," Berlin, 1910, p. 88, cited by Schwalbe, "Chemic der Cellulose," p. 620.

<sup>4</sup> *J. Ind Eng Chem.*, **9**, 561 (1917).

<sup>5</sup> Mahood, *Science*, **56**, 82 (1922), states that the concentration of chlorine rather than the temperature must be controlled in making the cellulose determination.

After the chlorine treatment, the shavings were treated with a solution of  $H_2SO_3$ , until the chlorine odor disappeared and were then transferred back to the alundum crucible and washed with hot water. Subsequently the shavings were again returned to the beaker and 100 cc of a 2 per cent sodium sulfite solution added and the beaker covered with a watch glass and placed in boiling water for 30 minutes. The partially delignified material was then transferred back to the crucible and thoroughly washed with water.

The treatment with chlorine, followed by the sulfite washing, was repeated until the fibers were practically white (i.e., until the chlorine-sulfite color reaction had disappeared). The Maule color reaction (following the interaction of wood with chlorine followed by  $Na_2SO_3$  treatment) has been discussed in a previous chapter. The disappearance of all but a faint coloration served as Schorger's end point. The later chlorination periods were always shorter than the original period. After lignin had been removed, the residue was given a final bleaching by the addition of 20 cc of 0.1 per cent  $KMnO_4$  solution, which after standing 10 minutes was decolorized by addition of  $H_2SO_3$ . The cellulose finally retained on the alundum crucible was washed thoroughly with hot water and then successively with aqueous acetic acid, alcohol, and ether. The crucible was dried for 2 hours at  $105^\circ C.$  in an air oven and weighed in a weighing bottle.

In general, Schorger found that the coniferous woods were more resistant to chlorination than were the hardwoods. Samples of Douglas fir, white spruce, longleaf pine, etc., required 4-5 chlorinations while yellow birch, basswood, and sugar maple required 2-3 chlorinations to effect delignification.

The time required in the Cross and Bevan chlorination (as described by Schorger) was investigated critically by Ritter and Fleck<sup>6</sup> who showed that prolonged chlorination was not particularly advantageous in removing lignin from finely divided wood samples. They made comparative studies (using 80-100 mesh material) by varying the periods of chlorination in two series. In the series of long chlorinations, successive time periods during which the chlorine made actual contact with the sample of wood, were 20, 15, 15, and 10 minutes. In the series of short chlorinations, the corresponding time periods were usually 5, 5, 5, and 5 minutes. The accompanying table (Table XII), which gives their results in brief, shows that the short time chlorinations serve in general to remove lignin and to cut down the degradation which cellulose suffers under the prolonged action of chlorine.

Later experiments by Ritter<sup>7</sup> showed that successive three minute

<sup>6</sup>J. Ind. Eng. Chem., 16, 147 (1924).

<sup>7</sup>J. Ind. Eng. Chem., 16, 947 (1924).

TABLE XII  
 COMPARISON OF CELLULOSE PREPARED BY SHORT AND LONG CHLORINATION PERIODS  
 (RITTER AND FLECK)  
 (Percentages based on oven-dry weight of material)

Species	Method of Chlorination	Chlorination Periods—Minutes	Cellulose in Wood	Pentosans in Cellulose	Lignin in Cellulose	$\alpha$ -Cellulose in Cellulose	$\beta$ -Cellulose in Cellulose	$\gamma$ -Cellulose in Cellulose
Eastern hemlock (sapwood)	Short	5, 5, 5, 5, 2	54.23	6.98	1.50	49.7	31.7	18.6
	Long	20, 15, 15, 10	54.76	6.15	1.30	45.3	33.8	20.9
(heartwood) .. . . .	Short	5, 5, 5, 5, 2	54.18	7.04	1.60	46.3	23.8	29.9
	Long	20, 15, 15, 10, 5	52.77	6.10	1.50	48.1	22.6	29.3
Black locust (heartwood). .	Short	5, 5, 5, 3	52.82	23.02	1.27	71.3	18.7	10.0
	Long	20, 15, 15, 10	51.91	24.76	1.32	45.0	32.0	23.0
Catalpa (heartwood) . . . .	Short	5, 5, 5, 5	55.33	21.68	0.95	73.7	7.6	24.7
	Long	20, 15, 15, 10	55.79	22.90	1.15	71.4	17.8	10.7

chlorinations instead of 5 minute periods proved sufficient to delignify wood. Ritter also showed that the partial gelatinization of Cross and Bevan cellulose could be eliminated by digesting the residue with hot water prior to the final washing.

A few other modifications of Cross and Bevan's original method deserve attention. Sieber and Walter<sup>8</sup> and later Johnsen and Hovey<sup>9</sup> carried out the reaction on a Gooch crucible so arranged that moist chlorine gas could be drawn through by suction. After the original chlorination and even during the sulfite treatment, the cellulose was never removed from the crucible. Manipulative losses were avoided in this way. Johnsen and Hovey also subjected their alcohol extracted wood sample to pretreatment (prior to chlorination) with a mixture of glacial acetic acid and glycerine in the proportion of their molecular weights (60:92). The finely divided wood sample was heated for several hours with this mixture at 135-40° in order to hydrolyze a part of the non-cellulosic polysaccharides of the cell wall. As a result of this preliminary treatment, the final cellulose yields are 3-4 per cent lower than those obtained without this pretreatment, but Johnsen and Hovey claim that the results are more nearly comparable to the cellulose (pulp) yields obtained in commercial pulping processes, that the actual cellulose of the cell wall is not attacked and that the residual cellulose has been partially freed from pentosans. This claim is substantiated by the previous work of Schwalbe and Johnsen.<sup>10</sup> However, the pretreatment of wood as suggested by Johnsen and Hovey has led to a lively polemic<sup>11</sup> which, while it requires no discussion, serves admirably in demonstrating the difficulty in clearly defining or delimiting the term *cellulose*, as applied to wood.

Dore's method for the determination of cellulose in wood is nearly identical with that of Sieber and Walter. The wood sample (about 2 grams), after extraction with various solvents (described in the preceding chapter) remains undisturbed in the same Gooch crucible from the start until the end of the analysis. The crucible is fitted with a filter plate sewn up between two layers of cotton fabric which has been carefully washed with water and alcohol. The filter plate (at the option of the analyst) may be fastened to the bottom of the crucible by means of a platinum wire. The wood sample rests on the filter plate. The assembled apparatus used by Dore<sup>12</sup> is shown in the accompanying cut (Figure 7). The Gooch crucible was supported over a suction filtering flask in the usual way. Around the filtration tube was fitted an inverted rubber stopper by means of which the crucible was capped with

<sup>8</sup> *Papierfabrikant*, 11, 1179, *C. A.*, 8, 1202 (1914).

<sup>9</sup> *Paper*, 21, No. 23, p. 40 (1918).

<sup>10</sup> *Pulp Paper Mag. Can.*, 13, 600 (1915).

<sup>11</sup> Johnsen, Mahood, Dore, *J. Ind. Eng. Chem.*, 12, 873 (1920); 13, 358 (1921).

<sup>12</sup> *J. Ind. Eng. Chem.*, 12, 264 (1920).

a glass adapter which served as the chlorine inlet. A moderately rapid stream of washed chlorine was drawn by suction through the wood sample for 20 minutes. The crucible was then removed and the sample treated with aqueous  $H_2SO_3$  and then washed with hot water. Following this, the crucible was placed in a 50 cc beaker, sufficient 3 per cent  $Na_2SO_3$  solution was added to nearly cover the material, and the beaker was heated on the steam bath for  $\frac{3}{4}$  of an hour. The crucible was then returned to its original position over the suction flask and sulfite solu-

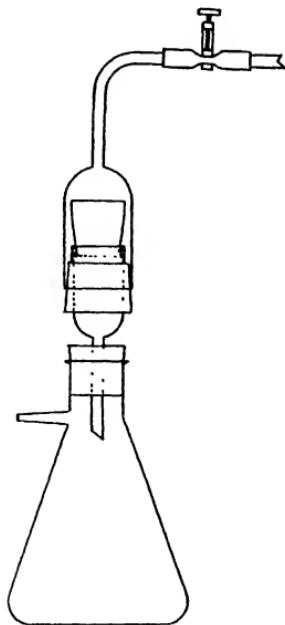


FIG. 7—Chlorination Apparatus used by Dore.

tion was poured through the residue which was then thoroughly washed with hot water. The chlorination and sulfite treatments were repeated several times (depending on the resistance of the wood towards delignification), the successive periods of chlorination being 15, 15, 15, and 10 minutes (etc.). After the last sulfite treatment, the material was again washed with hot water, dried 16 hours at  $100^\circ$ , and the crucible containing the cellulose weighed in a glass stoppered weighing bottle.

Renker's method as adopted by Schorger, and Sieber and Walter's method for cellulose determination have been described in detail, since

they are two of the most serviceable modifications of the original Cross and Bevan method now at the disposal of the chemist in forest products.

### Advantages and Limitations of the Chlorination Methods

The use of chlorine on finely divided wood, followed by treatment with sulfites insures practically the complete removal of those encrusting substances, which for want of a better name we have termed *lignin*. It also causes the removal of some of the more unstable polysaccharides which certain investigators group together under the hemicelluloses, although by no means *all* of these are removed. Preceded by adequate (not too drastic) treatment, it causes the removal of the extraneous substances like the tannins, dyes, resins, etc. However, the chlorination process alone never yields a homogeneous residue, nor one remotely approaching homogeneity. This homogeneity has been tacitly assumed by some chemists but it is contraverted by experimental facts. The process is based on the resistance of certain cell wall substances to attack by chlorine and on the removal of the non-resistant substances. No analytical method which functions by removing "impurities" from an insoluble residue can be free from criticism.

It is quite conceivable that an entire group of chemically different polysaccharides exist in the cell walls of certain woody plants that would be determined together as *wood cellulose*. It is also highly probable that among these substances there is one chemical individual (present in preponderating amount) that is identical with cotton cellulose in its chemical constitution.<sup>13</sup> In certain plants it is not unlikely that true cellulose can exist in such a physical state that its resistance to attack by chlorine would be considerably lowered and that it might be removed in part during chlorination and reckoned among the non-cellulosic constituents of the cell wall.

So much for the speculative side of the picture. Experiments have shown that slight variations or modifications in the chlorination method may cause startling changes in the properties of the "wood cellulose" residue. This is strikingly illustrated in two of Ritter and Fleck's analyses in which they compare the results of long and short period chlorinations.<sup>14</sup> Long period chlorinations in general gave lower yields of the resistant  $\alpha$ -cellulose. This same fact may be noted by contemplating the rapid increase in the alkali soluble portion of wood cellulose (or cotton cellulose) with repeated chlorinations. This is clearly shown in Table I, Chapter 1, Part II. These facts serve to weaken our confidence in the infallibility of the Cross and Bevan method, the results of which often

<sup>13</sup> For experimental evidence leading to this conclusion, cf Chapter 1, Part II, of this monograph.

<sup>14</sup> Cf.  $\alpha$ -cellulose determination in the case of black locust, Table XII.

become exceedingly difficult to interpret. We must recall that the method is a conventional one, that it is useful if properly standardized, and that it serves to determine quantitatively not *one individual component* of the cell wall in wood, but a group of components which share the general property of resistance to chlorination. If we must continue to speak of the residue after continued chlorination as "*cellulose*" it is well to qualify it by labelling it *Cross and Bevan cellulose* or *cellulose by the Cross and Bevan method*, so as to indicate the past history of the material and to differentiate it from cellulose fractions isolated from wood by other analytical methods.

### Analysis of Cross and Bevan Cellulose

*Furfural-Yielding Components* The fact that Cross and Bevan cellulose when treated with HCl yields furfural (or related aldehydes) has caused investigators frequently to determine furfural-yielding components in this cellulose residue, and arbitrarily to calculate the results as *pentosans*, *methyl pentosans*, or both, and to apply a correction to the percentage of Cross and Bevan cellulose. As a concrete example—the percentage of Cross and Bevan cellulose isolated from longleaf pine was approximately 58 per cent. The total pentosan and methylpentosan content in this residue (estimated from furfural determinations) was about 9 per cent. The corrected cellulose figure would then be  $(58 - (58 \times .09))$ , or 52.8 per cent. While this type of computation may give a truer estimate of the normal cellulose in wood, it is rather hazardous for the following reasons:

(a) The furfural, or related products may emanate (in part at least) from sources other than the pentosans, such as oxidation products formed from cellulose during the chlorination.

(b) The furfural or related products may be derived from substances which some chemists still contend are an integral part of "wood cellulose."

(c) Such a correction gives an incomplete picture, and hence misleading data on the true cellulose content of wood.

The first objection has been discussed previously (Chapter 2, Part II). The second one, the writers feel, is not in harmony with present day experimental evidence, but is presented for what it is worth. The third contention is justified, since there is experimental evidence that Cross and Bevan cellulose derived from conifers gives varying amounts of mannose as well as the pentoses on hydrolysis.

However, it is not quite proper to correct the cellulose content further by determining this mannose and calculating to *mannan*, and by subtracting this figure from the "pentosan-free" Cross and Bevan cellulose. The mannose (in the case of white spruce) may emanate in part from a carbohydrate that also gives other simple sugars on hydrolysis, and until the

constitution of such a complex polysaccharide is known, all corrections in the analysis of Cross and Bevan cellulose would be open to question. On the other hand, it has been shown that in individual cases the figures for "wood cellulose" determined by several totally different methods and subsequently corrected for "total pentosans and hexosans" were in good agreement.

While it is unsafe to make a correction for pentosans in the case of Cross and Bevan cellulose, it is always advisable to determine the furfural-yielding components in this residue. This is now the practice in the Forest Products Laboratory and results indicate that appreciable amounts of furfural-yielding material are always present in the cellulose fraction. Cross and Bevan celluloses from coniferous woods often yield a combined pentosan and methyl pentosan figure of 9-10 per cent. The cellulose residues from hardwoods not infrequently contain 2-2.5 times this amount.<sup>15</sup>

The studies of the Forest Products Laboratory have also shown that the Cross and Bevan cellulose from coniferous wood retains 38-56 per cent of the total furfural-yielding bodies of the original wood, and that the cellulose fraction from the hardwoods retains 57-66 per cent of these substances.

Pretreatment of the wood with glycerine-acetic acid mixtures prior to the Cross and Bevan determination lowers the amount of pentosans in the cellulose residue<sup>16</sup> but it does not remove the major portion of the furfural-yielding substances.

*Ash.* The ash retained by Cross and Bevan cellulose is usually slight. From Schorger's results it would appear that this ash content seldom rises above 0.4 per cent and is usually well under this figure.

*Lignin.* Small amounts of lignin are often tenaciously retained by Cross and Bevan cellulose. To determine whether such lignin is present it is well to test the solubility of the cellulose in 72 per cent  $H_2SO_4$ . If the residue is appreciable, it should be filtered off after diluting with water, washed and weighed, and subtracted as a correction from the total Cross and Bevan cellulose.

*Alpha, Beta and Gamma Cellulose.* In a previous chapter we briefly defined the terms  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cellulose as they are commonly used.

Schwallbe<sup>17</sup> who applied these determinations to pulp has described them as follows:<sup>18</sup> Ten grams of the cellulose residue are thoroughly incorporated into 50 cc of 17-18 per cent  $Na(OH)$  and the mixture is allowed to stand for 30 minutes. It is then treated with 50 cc water,

<sup>15</sup> Cf. Table XIX, Chapter 6, Part III.

<sup>16</sup> Johnsen and Illovey, *loc. cit.*

<sup>17</sup> "Chemic der Cellulose," p. 637 (1911).

<sup>18</sup> Cf. also Cross and Bevan, "Researches on Cellulose," 3, p. 23 (1905-10); and Jentgen, *Kunststoffe*, 1, 165 (1911).

stirred and filtered off by suction on a Büchner funnel and washed with small successive portions of cold water until the filtrates are no longer alkaline. These filtrates are kept separate from subsequent washings. The residue which is washed with hot water is dried and weighed. This residue is the resistant portion of the Cross and Bevan cellulose and is usually termed  $\alpha$ -cellulose.

The *alkaline* filtrates from the  $\alpha$ -cellulose are treated with concentrated acetic acid until the solution is distinctly acid. This precipitates the so-called  $\beta$ -cellulose which is heated at 100° until the mother liquors are clear and the precipitate settles readily. The  $\beta$ -cellulose is then filtered, washed with 6-8 portions of boiling water, dried and weighed. The difference between the total cellulose and the sum of the  $\alpha$ - and  $\beta$ -cellulose is known as  $\gamma$ -cellulose [i.e., "Cross and Bevan cellulose"--( $\alpha$ -cellulose +  $\beta$ -cellulose) =  $\gamma$ -cellulose].

Quite recently, Bray and Andrews<sup>10</sup> stimulated by the difficulties met with in the above procedure, devised a volumetric method for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cellulose. The claims for this method are (1) that it is more rapid than the gravimetric analysis, (2) that it overcomes washing and filtration difficulties and (3) that since aliquot portions are used, check determinations may be made without retracing all the steps of the analysis.

The method which may be applied to pulp as well as to Cross and Bevan cellulose depends on the quantitative oxidation of cellulose to  $\text{CO}_2$  by means of dichromate:  $\text{C}_6\text{H}_{10}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 5\text{H}_2\text{O}$ .

"Since the potassium dichromate solution is to be used in oxidizing cellulose from pulps, it is standardized against cellulose obtained by the chlorination method of Cross and Bevan from sulfite pulp. The cellulose equivalent so obtained is used in preference to the theoretical value.

"Approximately 1 gram of cellulose (not corrected for ash), dried at 105° C., is taken from a weighing bottle and placed in a 250-cc beaker. This is triturated with 30 cc of 72 per cent sulfuric acid and allowed to stand until solution is complete. The sulfuric acid solution is transferred to a 100-cc graduated flask. The beaker is washed several times with 72 per cent sulfuric acid to insure complete removal of the dissolved cellulose. The flask is filled to the mark with 72 per cent sulfuric acid and thoroughly mixed. To a 10-cc portion of the dissolved cellulose, 10 cc of potassium dichromate solution (containing approximately 90 grams per liter) and approximately 60 cc of 72 per cent sulfuric acid are added. The solution in the beaker is boiled for exactly 5 minutes, cooled in ice, and titrated with ferrous ammonium sulfate solution (containing 159.9 grams per liter), using potassium ferricyanide as an indicator. The titration is conducted in the usual way and the point where a drop of the titrated solution gives a blue color with a drop of the indicator is taken

<sup>10</sup> *Ind. Eng. Chem.*, 15, 377 (1923).

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"Approximately 1 gram of cellulose (not corrected for ash), dried at 105° C., is taken from a weighing bottle and placed in a 250-cc beaker. This is triturated with 30 cc of 72 per cent sulfuric acid and allowed to stand until solution is complete. The sulfuric acid solution is transferred to a 100-cc graduated flask. The beaker is washed several times with 72 per cent sulfuric acid to insure complete removal of the dissolved cellulose. The flask is filled to the mark with 72 per cent sulfuric acid and thoroughly mixed. To a 10-cc portion of the dissolved cellulose, 10 cc of potassium dichromate solution (containing approximately 90 grams per liter) and approximately 60 cc of 72 per cent sulfuric acid are added. The solution in the beaker is boiled for exactly 5 minutes, cooled in ice, and titrated with ferrous ammonium sulfate solution (containing 159.9 grams per liter), using potassium ferricyanide as an indicator. The titration is conducted in the usual way and the point where a drop of the titrated solution gives a blue color with a drop of the indicator is taken

\* *Ind. Eng. Chem.*, 15, 377 (1923).

as the end-point of the titration. The relative value of ferrous ammonium sulfate solution to the dichromate solution is established by titration in the usual way.

"One gram of dry Cross and Bevan cellulose or sample of pulp is weighed into a 250-cc beaker and triturated with 25 cc of mercerizing liquid (17.5 per cent sodium hydroxide solution) until the mass is homogeneous, and allowed to stand for 30 minutes. The contents of the beaker are filtered with suction through an alundum (porosity R. A. 98) or a Gooch crucible. After the insoluble cellulose is sucked practically dry, it is loosened with a glass rod and washed, first with 4 per cent sodium hydroxide solution (50 cc) and then with approximately 300 cc of cold distilled water in small quantities.

"Since the  $\alpha$ -cellulose is dissolved in 72 per cent sulfuric acid, it is not necessary to wash it free from sodium hydroxide, which would be very difficult to remove in cellulose containing a high percentage of  $\beta$ -cellulose. In some cases it is impossible to separate the alkali-insoluble and alkali-soluble cellulose ( $\alpha$ - and  $\beta$ -cellulose) by filtration through an alundum crucible, as the cellulose mass becomes very jelly-like because of the presence of  $\beta$ -cellulose. In such cases the alkali-treated cellulose is placed in tubes and centrifuged until the  $\alpha$ -cellulose separates at the bottom of the tube. The supernatant liquid is decanted from the  $\alpha$ -cellulose which is successively washed by decanting and centrifuging, first with 4 per cent sodium hydroxide solution (50 cc) and then with distilled water, until the total washings approximate 350 cc.

$\alpha$ -Cellulose—The alkali-insoluble or  $\alpha$ -cellulose is removed from the alundum crucible with a pointed glass rod and placed in a 250-cc beaker. The filtrate is used for the  $\beta$ - and  $\gamma$ -cellulose determination. It is then dissolved in approximately 30 cc of 72 per cent sulfuric acid, transferred to a 100-cc graduated flask by washing successively with portions of the acid, and filled to the mark. A 10-cc sample is pipetted into a 250-cc Pyrex beaker, to which are added 10 cc of standard dichromate solution and approximately 60 cc of 72 per cent sulfuric acid. The oxidizing mixture is boiled gently for exactly 5 minutes and cooled in ice, and the excess dichromate is titrated with ferrous ammonium sulfate solution, as described under the standardization of potassium dichromate solution.

$\beta$ - plus  $\gamma$ -Cellulose—The 350-cc alkaline filtrate containing the  $\beta$ - and  $\gamma$ -cellulose, remaining from the alkali-insoluble or  $\alpha$ -cellulose determination, is diluted to exactly 400 cc. This is divided into two equal parts. One 200-cc portion, which is left alkaline, is diluted to 150 cc in a graduated flask. A 25-cc portion of this solution is pipetted into a 250-cc beaker. To this are added 5 cc of the standard dichromate solution and 60 cc of 72 per cent sulfuric acid. The contents of the beaker are boiled for exactly 5 minutes, cooled in ice, and titrated as described under the

$\alpha$ -cellulose determination. From this titration the sum of the percentages of  $\beta$ - and  $\gamma$ -cellulose is calculated.

" $\gamma$ -Cellulose"—The remaining 200 cc of the alkaline filtrate from the  $\alpha$ -cellulose determination are acidified with 10 per cent sulfuric acid solution, using one drop of dilute methyl orange as indicator, adding 5 cc of the acid in excess, and diluting to 250 cc in a graduated flask. This procedure almost immediately precipitates the  $\beta$ -cellulose. The flask is allowed to stand for several hours, or until the  $\beta$ -cellulose coagulates and settles to the bottom. A 25-cc portion of the supernatant liquid is pipetted from the flask and treated as described under the  $\beta$ - plus  $\gamma$ -cellulose determination. From this determination the percentage of  $\gamma$ , or soluble, cellulose may be calculated.

" $\beta$ -Cellulose"—The percentage of  $\beta$ -cellulose is obtained by subtracting the result of the  $\gamma$ -cellulose determination from the result of the  $\beta$ - plus  $\gamma$ -cellulose determination."

While  $\beta$ -cellulose and  $\gamma$ -cellulose are usually removed from  $\alpha$ -cellulose by means of 17.5 per cent alkali, this operation has been carried out arbitrarily without recourse to reliable solubility data of cellulose in NaOH. Very recently D'Ans and Jager<sup>20</sup> have reported that cellulose of different origins (chemical pulps, cotton cellulose, viscose, etc.) all show a maximum solubility at 23° in 12 per cent NaOH (by volume), irrespective of the actual amount of substance dissolved at this point. At higher concentrations of alkali, the solubility of cellulose rapidly decreases and apparently the alkali derivatives of  $\beta$ - and  $\gamma$ -cellulose become less and less soluble. In the light of these data it would seem reasonable to experiment with the lower concentration of alkali (with rather carefully controlled temperature conditions) in any future study of the  $\alpha$ ,  $\beta$ , and  $\gamma$ -cellulose determination. Furthermore, since it is quite probable that cellulose is oxidized in air in alkaline suspension, it would appear advisable to carry out the reaction in an atmosphere of an inert gas.

The significance of the terms  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cellulose has been discussed previously. In a carefully standardized scheme of analysis<sup>21</sup> these terms possess a certain practical significance in showing the relative resistance to alkali of various Cross and Bevan residues. If, however, the terms are stretched beyond their elastic limit and an attempt is made to establish these fractions as chemical entities which occur in the original wood, they lose their meaning. Of the three fractions,  $\alpha$ -cellulose (isolated from coniferous woods), while it still retains extraneous material, most closely approaches cotton cellulose in its chemical properties. As we have shown in Chapter 1, Part II, accumulating experimental data serve to show that

<sup>20</sup> *Cellulosechemie*, 6, 144 (1925).

<sup>21</sup> The Cellulose Division of the American Chemical Society is working towards such a standard method of analysis.

the  $\alpha$ -cellulose from wood and normal cellulose from cotton probably contain the same cellulose unit. The fact that  $\alpha$ -cellulose still retains small quantities of furfural-yielding material does not militate against this hypothesis, despite the criticisms of some recent investigators.<sup>22</sup> In the opinion of the writers, the question is still an open one with *preponderating experimental evidence in favor of the chemical identity of the larger part of the substance of  $\alpha$ -cellulose of wood with  $\alpha$ -cellulose isolated from cotton.*

The terms  $\beta$ - and  $\gamma$ -cellulose are really misnomers. The names might imply that they are isomeric with  $\alpha$ -cellulose but we have no experimental basis for such an assumption. They may include substances related to cellulose or they may contain degradation products of cellulose. Their origin is never certain. We do know that if we keep on rechlorinating Cross and Bevan cellulose indefinitely, we obtain accumulating  $\beta$ - and  $\gamma$ -cellulose fractions at the expense of the  $\alpha$ -cellulose. This in itself indicates that only under rigorously standardized conditions can we expect comparable results in the fractional analysis of Cross and Bevan cellulose.

### Other Methods Used in Determining Cellulose in Wood

Renker<sup>23</sup> deserves the credit for making a comparative study of the various methods for determining cellulose in wood and of emphasizing the utility of the Cross and Bevan method.

In the accompanying table (Table XIII) we have compiled the results of some of Renker's investigations (summarized by Schwalbe) which indicate pretty clearly that total cellulose yields in wood and cotton depend largely on the methods employed.

The report of the International Commission on Analysis of 1909<sup>24</sup> emphasizes this same point and furthermore shows that an individual method of analysis applied to a given sample gives varying results in the hands of different analysts.

TABLE XIII  
YIELDS OF CELLULOSE OBTAINED FROM WOOD AND FROM COTTON BY VARIOUS ANALYTICAL METHODS (RENKER)

Method Used	Per Cent Cellulose in Wood	Per Cent Cellulose in Cotton
Cross and Bevan method	60.55	97.85
Muller's bromine water method	57.95	97.1
Klason's modification of Muller's method	51.85	95.45
Schulze-Henneberg $HNO_3 - KCIO_3$ method	58.1	96.95
HCl and $KClO_3$ method	57.15	96.15
$KMnO_4$ and HCl method	43.0	96.65
$NaClO$ method	50.5	96.8
Phenol method (German Pat. No. 94467)	51.9	94.2

<sup>22</sup> Ritter and Fleck, *J. Ind. Eng. Chem.*, **14**, 1050 (1922).

<sup>23</sup> *Loc. cit.*

<sup>24</sup> Cf. Schwalbe's "Chemie der Cellulose"

Methods other than those involving chlorination will be discussed very briefly. Many of them have proved too cumbersome to be practical, while a number of them deserve further study.

Hugo Müller's cellulose determination<sup>25</sup> depends on the treatment of alcohol and benzene extracted material with a 1.25 per cent solution of bromine in water. Small successive amounts of this reagent are added as long as the bromine reacts with lignin. The end point is reached when a small portion of the reagent is no longer decolorized. The residue is then washed with water and treated with aqueous ammonia, again washed and retreated with the bromine water until decolorization again ceases. These alternate treatments with bromine water and ammonia are continued until a pure white product is obtained which fails to react further with bromine even after ammoniacal treatment. Muller's method, while giving fairly reliable results, is obviously very time-consuming. Klason<sup>26</sup> modified Müller's method by treating wood samples at 108° C. with  $\text{Ca}(\text{HSO}_4)_2$  (0.5*N*  $\text{CaSO}_4$  and 0.6*N*  $\text{SO}_4^{2-}$ ) prior to the action of bromine water. However, as shown in Table XI11, the results are quite low.

An old method for the determination of cellulose, devised by F. Schulze and modified by Ilenneberg<sup>27</sup> depends on the gradual interaction of wood with a mixture of 0.8 part  $\text{KClO}_3$  and 1.2 parts of 17 per cent  $\text{HNO}_3$  (*d*.1.1), at 15° or under. The reaction may require over two weeks (at times eight weeks) before a sufficiently "pure" cellulose fraction is obtained. At the end of the reaction the product is washed, treated with ammonia and finally with water. Besides its obvious tediousness, Schulze's method, in Renker's hands, gave fluctuating results which were often low. Oxidation products (such as "oxycellulose") were found in the residue, and the method was shown to be impractical.

The Schulze method was also modified by Hoffmeister<sup>28</sup> who used a mixture of  $\text{KClO}_3$  and  $\text{HCl}$ . By this means lignin could be removed in 24-36 hours but the residue contained a higher percentage of oxidation products than did the cellulose obtained by the original procedure.

Hagglund and Grenquist<sup>29</sup> have attempted to isolate and determine cellulose by carefully regulating the hydrogen-ion concentration of their sulfite cooking liquor so as to leave cellulose unaffected while removing lignin and the pentosans. Such a cooking liquor contained 80 grams  $\text{NaHSO}_3$  in one liter of 0.2*N*  $\text{HCl}$ . This liquor also fails to destroy the glucose formed on hydrolysis of the "hemicelluloses" of wood. By allowing this reagent to react with spruce wood for 7-8 days, a cellulose yield of

<sup>25</sup> "Pflanzenfaser," pp. 27-28.

<sup>26</sup> Cf. Schwalbe, "Chemie der Cellulose," p. 621.

<sup>27</sup> Ann., 146, 130 (1868).

<sup>28</sup> Landw. Jahrb., 17, 240 (1888).

<sup>29</sup> Middelungen Abo Akademie Inst fur Trakemi, No. 1 (1922), through Cellulosechemie, 4, 90 (1923).

55 per cent was obtained. This compares favorably with yields of Cross and Bevan (spruce) cellulose after pentosan corrections have been made. While the procedure is probably valuable in serving as a standard for sulfite cooking operations, it is too long to warrant its use in the determination of cellulose.

The cellulose determination by means of phenol, originally devised by Bühler (German Patent No. 94467) has recently been reinvestigated by Kalb and Schoeller.<sup>30</sup> Four gram samples of extracted wood were treated for several hours with 50 grams of phenol and 25 to 200 milligrams HCl, at temperatures ranging from 60 to 97° C. The mixture was then washed successively with water, aqueous NaOH, water, dilute acetic acid and water. The results are consistent and reproducible but usually lower than those obtained by the Cross and Bevan method. Some of the polysaccharides of the cell wall which remain in Cross and Bevan cellulose appear to be hydrolyzed by the treatment with phenol. HCl (or some other catalyst, like the halogens) is indispensable in the phenol delignification of wood.<sup>31</sup> Phenol alone is a poor delignifying agent.<sup>32</sup>

A method that has recently been applied to the determination of the entire "skeletal tissue of the cell wall" is the ClO<sub>2</sub>-Na<sub>2</sub>SO<sub>3</sub> method devised by E. Schmidt and his co-workers. This method of isolating the resistant polysaccharides of the cell has been discussed in a previous chapter. Schmidt has really defined lignin as that part of the woody tissue which is attacked and removed by ClO<sub>2</sub>. Any sugar-yielding components that are removed in this way, he claims, belong properly with the encrusting substances of wood. Heuser and Merlau<sup>33</sup> have made a careful study of Schmidt's method and have compared its results with those obtained by the Cross and Bevan procedure. Extracted samples in the form of air-dried wood flour were shaken intermittently during 24 hours with an excess of 1.5 per cent ClO<sub>2</sub> solution. The residue was then filtered on a Gooch crucible and washed with warm water until the ClO<sub>2</sub> reaction had disappeared (KI indicator). The material on the filter paper was washed repeatedly with 2-3 per cent Na<sub>2</sub>SO<sub>3</sub> solution until the washings were clear. Then followed successive washings with warm water, 0.2N ClO<sub>2</sub> solution and water. The residue after drying at 100° was termed the "skeletal substance" of wood. The results are considerably higher than those obtained for cellulose by the Cross and Bevan method. Heuser contends that this skeletal substance must be considered a "crude cellulose" residue ("Rohcellulose") since in the case of spruce wood it contains appreciable amounts of pentosans and mannans. On the other

<sup>30</sup> *Cellulosechemie*, **4**, 37 (1923).

<sup>31</sup> Legeler, *Cellulosechemie*, **4**, 61 (1923).

<sup>32</sup> For a very recent and comprehensive study of the action of various phenols on wood and lignin, cf. A. Hillmer, *Cellulosechemie*, **6**, 169 (1925).

<sup>33</sup> *Cellulosechemie*, **4**, 101 (1923).

hand, the residue does not retain *all* of the pentosans since the ClO<sub>2</sub> treatment which is practically without effect on cellulose causes the removal of small amounts of pentosans. According to Heuser, then, the method furnishes no gauge of the total polysaccharide content of the cell wall, although it approaches such a result more closely than do other analytical procedures. If pentosans and mannans in the cellulose are determined and the yield of "pure cellulose" (Reincellulose) is calculated, the results are nearly identical with the yield of Cross and Bevan cellulose *corrected for pentosans and mannans*. Heuser's results are shown in Table XIV. It is obvious that unless such corrections are made, the two methods do not yield directly comparable results.

Heuser has demonstrated that the ClO<sub>2</sub> method may be very useful. The technic does not require much of the analyst's time and frequent retreatments of the "skeletal" residue are unnecessary. Special precautions, however, must be taken in the preparation of the ClO<sub>2</sub> reagent to avoid explosions.<sup>34</sup>

TABLE XIV  
YIELDS OF CELLULOSE FROM SPRUCE WOOD (HEUSER AND MERITI)

	Pentosan in Cellulose; Per Cent Based on Total "Crude" Cellulose	Mannan in Cellulose, Per Cent Based on Original Wood	Corrected Per Cent Cellulose
Cross and Bevan method	59.24	4.90	52.28
Schmidt's ClO <sub>2</sub> method	62.71	4.44	52.84

### Indirect Methods for Cellulose Determination

In their study of the components of wood and their industrial value, Konig and Becker<sup>35</sup> used a summative analysis in which they determined cellulose by difference. They subtracted from 100, the percentages found for protein, resin, ash, lignin, and "hemicelluloses." (The latter included hexosans and soluble pentosans.) This difference was termed "crude cellulose" which was then corrected for "insoluble pentosans." (The latter are the furfural-yielding substances which remain unhydrolyzed after treatment of the wood sample with very dilute H<sub>2</sub>SO<sub>4</sub> under pressure.) The result of such a correction is the "pure cellulose." The yield figures obtained in this way are hardly comparable with those obtained by chlorination. The cellulose yields by Konig and Becker's

<sup>34</sup> The orange-colored gas is generated by mixing oxalic acid with KClO<sub>3</sub>, cooling the solution and treating the mixture with cold aqueous H<sub>2</sub>SO<sub>4</sub>. This insures the presence of CO<sub>2</sub> as a diluent of the explosive ClO<sub>2</sub>. The gas is absorbed in Wolff bottles containing ice-cold water.

<sup>35</sup> Z. angew. Chem., 32, 155 (1919).

method are much lower, ranging from about 40-50 per cent and never exceeding the higher figure.<sup>36</sup>

Other methods that have been proposed for the determination of cellulose in woods, all of which give much lower results than does the chlorination process without offering any marked advantages in technic, require no discussion.

<sup>36</sup> Cf. Chapter 6, Part III, of this monograph.

## Chapter 4

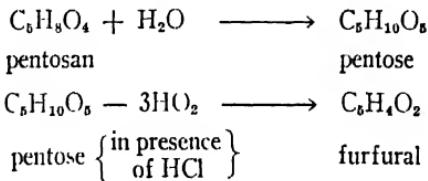
# The Determination of Pentosans and Hexosans in Wood

### The Pentosan Determination

Perhaps no analytical methods that have been applied to plant tissues have aroused greater interest than those used in the determination of pentosans. Within the past few years these methods have been subjected to careful study and, at the time of writing (1925), European chemists are reinvestigating the entire subject in the light of new data that have been published since the original methods were devised and in the hope of overcoming some inherent difficulties of the standardized procedures now in vogue. The Cellulose Division of the American Chemical Society has also appointed a committee to study pentosan methods.

A full critique and historical review of the pentosan determination would be beyond the scope of this monograph. They have been given admirably in a series of articles by Pervier and Gortner<sup>1</sup> to which reference is made.

Pentosans cannot be determined directly. Their quantitative estimation depends on their conversion into pentose sugars and subsequently into furfural by the action of HCl.



The gravimetric method for furfural, now in common use, was probably first devised by Councill<sup>2</sup> and later studied and modified by a host of investigators among whom Tollens and his students played an important part. The method depends upon the precipitation of furfural phloroglucide from a hydrochloric acid distillate by means of phloroglucinol. This analytical procedure was applied by Schorger to the analysis of

<sup>1</sup>Ind. Eng. Chem., 15, 1167 and 1255 (1923).

<sup>2</sup>Chem. Ztg., 18, 966 (1894).

wood at the Forest Products Laboratory and his technic (which is given in detail) is now in general use.<sup>3</sup>

"Two grams of sawdust from coniferous wood (1 gram from hardwoods) are placed in a 250 cc flask provided with a separatory funnel and attached to a condenser. (The flasks are easily made by fusing an outlet tube and funnel to the ordinary all glass wash bottles.) Add 100 cc of 12 per cent hydrochloric acid (specific gravity 1.06) and distil at the rate of 30 cc in 10 minutes. The distillate is passed through a small filter before entering the receiver. As soon as 30 cc of distillate are collected, 30 cc of HCl are added to the distillation flask and the distillation is continued in this manner until 360 cc of distillate are collected. To the total distillate add 40 cc of filtered phloroglucine solution (that has been prepared at least a week previously by heating 11 grams of phloroglucine in a beaker with 300 cc of 12 per cent HCl and after solution has taken place, making up to 1,500 cc with 12 per cent HCl). After addition of the phloroglucine, the solution soon turns greenish black. After standing 16 hours, the furfural phloroglucide will have settled. If a drop of the supernatant liquid gives a pink color with aniline acetate paper, the precipitation of the furfural is incomplete. A further amount of phloroglucine solution is then added and the beaker allowed to stand overnight as formerly.

"The furfural phloroglucide is filtered, using a tared Gooch crucible having a thick asbestos mat, and washed with exactly 150 cc of H<sub>2</sub>O. The crucible is then dried for 4 hours in a water bath and weighed in a weighing bottle."

The weight of material, however, does not represent only furfural phloroglucide. It includes the insoluble phloroglucides of any other related aldehydes that may have been formed from wood by the action of HCl. Such compounds might include methylfurfural and hydroxymethyl furfural. Schorger assumed the presence of methylfurfural and adapted his procedure as follows:

"The crucible (containing the dried phloroglucides) is placed in a narrow beaker and 20 cc of 95 per cent alcohol are added to the crucible. The beaker is then placed in a water bath maintained at 60° for 10 minutes. The alcohol is removed with a suction pump and the process repeated (usually 4 or 5 times) until the alcohol that runs through is practically colorless. The crucible is then dried for 2 hours in the water oven and again weighed. The weight of the residual phloroglucide subtracted from the weight of the mixed phloroglucides gives the weight of the methylfurfural phloroglucide."

<sup>3</sup> In 1894, DeChaniot, *Am. Chem. J.*, 16, 224, determined the furfural obtained from a number of hardwoods and conifers on treatment with HCl by precipitating the furfural as the phenylhydrazone.

The amounts of pentosan and methylpentosan may then be calculated by the use of Kröber's tables<sup>4</sup> and the data of Ellett and Tollens.<sup>5</sup>

The technic in the phloroglucinol method could probably be improved in accordance with the suggestions of Schwalbe who carefully standardizes the dimensions of his distillation flasks, outlet tubes, etc., and to insure regular distillation of the furfural, recommends heating the flask in an oil bath at 160° C.<sup>6</sup>

Pervier and Gortner, however, have raised serious objections to the entire phloroglucinol method. They have shown experimentally<sup>7</sup> that the distillation of pentose-yielding materials takes place, not in the presence of the 12 per cent HCl originally added to the distillation flask, but in contact with 18-20 per cent HCl. At this concentration HCl partially destroys the furfural, and the analytical results are therefore low. They claim that by modifying the distillation as follows, this destruction of furfural is prevented: A weighed sample is mixed with 200 cc of 12 per cent HCl hydrochloric acid in a 750 cc distilling flask fitted up for steam distillation. A slow current of steam is conducted into the mixture which as soon as it reaches the boiling point is heated with a low flame so that the vapor in the neck of the distilling flask is regularly maintained at 103-5° C. About half of the original volume of the liquid should remain in the flask at the end of the distillation, which is continued until the distillate no longer reddens aniline paper.

Objections to the phloroglucinol method, raised by Pervier and Gortner, and others, may be summarized as follows:

1. The method is not based on the molecular weight of the precipitate which (judging from the divergent analytical data of different observers) has no fixed chemical composition. The entire procedure is therefore empirical.

2. Solubility corrections for the phloroglucide precipitate are required.

3. The different pentoses yield varying amounts of furfural, thus necessitating the use of a specific factor for computing a specific sugar and an empirical mean factor for computing "pentosans." In the case of woods, this last named factor is presumably unreliable.

4. Substances other than pentosans may yield furfural by the HCl distillation method.

5. Phloroglucinol precipitates substances other than furfural.

Despite these valid objections against the method, it is difficult to find a procedure that will do away with all of them.

The methylpentosan determination included by Schorger is open to very serious question. There is no experimental evidence that methyl

<sup>4</sup>Cf. U. S. Dept. Agriculture Bulletin 107 (Revised), pp. 226-30 (1908).

<sup>5</sup>Ber., 38, 492 (1905)

<sup>6</sup>Schwalbe-Sieber, "Betriebskontrolle," p. 80.

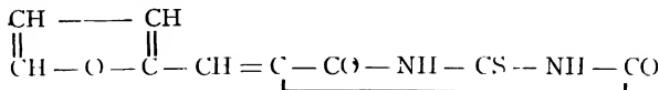
<sup>7</sup>Loc. cit.

pentosans or methylfurfural-forming substances are present in most woods. (Exceptions are found in a few woods like fustic (*Rhus cotinus*) which has been shown to contain the rhamnoside *fustin*). Nevertheless nearly all woods hitherto examined appear to give rise to appreciable amounts of methylfurfural when the usual analysis is carried out. Tanbark oak (*Quercus densiflora*)<sup>8</sup> wood is an interesting exception to this general rule. The non-formation of alcohol-soluble phloroglucides in the case of this wood remains unexplained.

The methylpentosan determination becomes even more questionable when we consider that purified hexoses and hexosans that are incapable of yielding methylfurfural, apparently give rise to methylfurfural by Schorger's method. If we treat purified cellulose, starch, glucose, fructose, mannose, etc., with HCl under the conditions of Schorger's pentosan analysis, we invariably obtain small but appreciable amounts of a precipitate with phloroglucinol. This precipitate is always partially soluble in alcohol and this soluble portion would therefore be mistaken for methylfurfural phloroglucide. In fact the amounts of these alcohol soluble phloroglucides are of the same order of magnitude as the amounts obtained from some of our native woods, when the methylpentosan determination is made.<sup>9</sup> Pure hexoses do not yield methylfurfural. The phloroglucide precipitates are probably due to hydroxymethylfurfural, which, as Heuser and his co-workers have shown, emanates from the action of acids on cellulose.<sup>10</sup> Unless it has been proved that an individual wood yields methylpentoses on hydrolysis (as shown by actual isolation of the sugar or its derivatives) the methylpentosan analysis is of no help whatsoever in determining the presence or amount of such substances in the original wood, and is therefore quite worthless.

A number of other gravimetric methods for the determination of furfural have been proposed and among these, methods depending on the use of barbituric acid derivatives have received a good deal of attention.<sup>11</sup> The methods were recently studied by Dox and Plaisance.<sup>12</sup> They found it possible to determine furfural quantitatively in the presence of 12 per cent HCl by means of thiobarbituric acid CO — NII — CS.NH — CO — CH<sub>2</sub>

which forms a condensation product having the definite structure:



<sup>8</sup> Cf. Table XIX.

<sup>9</sup> Vanselow and Wise; unpublished data on the methylpentosan determination.

<sup>10</sup> Cellulosechemie, 4, 25 and 85 (1923).

<sup>11</sup> Cf. Bibliography of Pervier and Gortner, *loc. cit.*

<sup>12</sup> J. Am. Chem. Soc., 38, 2156 (1916).

This product is formed under conditions very similar to those obtaining in the phloroglucinol method and no solubility correction is required. Barbituric acid,  $\text{CO} - \text{NH} - \text{CO} - \text{NH} - \text{CO} - \text{CH}_2$ , gave low results

unless a large excess of reagent was used. Thiobarbituric acid also reacts with methylfurfural and so this substance and furfural would be determined together if methylpentosans and pentosans were originally present. The thiobarbituric acid method is worthy of further study in the analysis of woods, since it involves the synthesis of a definite condensation product which is practically insoluble in HCl.

Recently Gierisch<sup>18</sup> has completed another critical study of the pentosan method as applied to wood. He preceded his quantitative studies by a series of carefully correlated color reactions which gave strong evidence that the 12 per cent HCl distillate contained appreciable amounts of hydroxymethylfurfural. He obtained no qualitative evidence for the presence of methylfurfural but states that its *absence* was never satisfactorily proved. The hydroxymethylfurfural comes partly from the degradation of "hemicellulose hexosans" and in part (as the distillation proceeds) from the decomposition of wood cellulose. Since the phloroglucide method causes the precipitation of hydroxymethylfurfural as well as furfural, and since the barbituric acid method fails to precipitate more than relatively small amounts of hydroxymethylfurfural, Gierisch recommends the latter method in wood analysis. He also points out that the precipitated phloroglucides, after extraction with alcohol, do not give residues that represent *only* furfural phloroglucide, since an appreciable amount of the hydroxymethylfurfural phloroglucide is insoluble in alcohol under the conditions of extraction. Differences between the results obtained with the two methods are shown in Table XV. Gierisch does not seem to have repeated the work of Dox and Plaisance by using the thiobarbituric acid procedure.

TABLE XV  
FURFURAL YIELDS BY THE PHLOROGLUCIDIC AND BARBITURIC ACID METHODS.  
COMPARATIVE DATA OBTAINED BY GIERISCH

Wood Sample	Per Cent Furfural	
	Calculated from the Alcohol-Insoluble Phloroglucide	Calculated from the Condensation Product with Barbituric Acid
Beech .....	13.70	12.53 11.85
Spruce .....	5.13 4.96	—
Spruce .....	4.90 5.08	4.68 4.85

<sup>18</sup> *Cellulosechemie*, 6, 61 (1925).

Of the volumetric methods that have been proposed, only two need be mentioned briefly. Pervier and Gortner<sup>14</sup> proposed a method which follows: To the distillate of furfural (containing 0.1-0.2 gram of furfural) 5 cc of a 20 per cent KBr solution are added for every 100 cc of solution and the acidity so adjusted that about 4 per cent HCl is present. With continual stirring 0.1 N  $KBrO_3$  is run in from a buret at a rate that will avoid a distinct yellow color throughout the solution. When the end point is approached a pale yellow color will be apparent immediately after the addition of a few drops of the bromate solution. This color soon fades. The bromate is then added in 0.25 cc increments and a record is kept of the time required for the disappearance of free bromine. This is done by the use of a simple galvanometer set-up, and a stop-watch.<sup>15</sup> As the end point is crossed a large increase in the time required is noted and the observations are carried somewhat beyond this point. The ratios  $dt/dv$  (where  $dv$  is the increment of bromate added and  $dt$  is the increase in time required for its disappearance over that required by the preceding increment) are then plotted against the total volume of bromate solution used and a curve is obtained which passes through a maximum at the end point. The total number of cc of 0.1 N bromate required to reach the end point  $\times 0.004803 =$  grams of furfural in the distillate. Pervier and Gortner's method is rapid and gives accurate results for furfural and pentosans. Hydroxymethylfurfural interferes so slightly with the reaction that it may be disregarded. Levulinic acid, a decomposition product of the hexoses, is without effect. Methylfurfural, however, reacts with the bromate solution and if present gives rather high values (107 per cent of the theoretical). These would give rise to an appreciable error in the determination of pentosans which were admixed with methylpentosans. To the best of our knowledge, Pervier and Gortner's method has not yet been applied to woods.

A somewhat different procedure, also involving the use of a bromate solution, has been described by Powell and Whittaker.<sup>16</sup> The method depends on the interaction of 4 atoms of bromine with 1 molecule of furfural in HCl. The furfural distillate obtained by distilling wood with 12 per cent HCl is diluted to 500 cc. Twenty-five cc of a standard 0.1 N  $NaBr-NaBrO_3$  solution are placed in each of four well stoppered flasks and 200 cc of the furfural distillate are added to each of two of these. To each of the two others (controls) are added 200 cc of 12 per cent HCl. The stoppered flasks are allowed to stand for one hour in the dark. Ten cc of 10 per cent KI solution are then added and the liberated iodine is titrated with 0.1 N sodium thiosulfate solution. The number

<sup>14</sup> Loc. cit.

<sup>15</sup> Described in detail in *Ind. Eng. Chem.*, 15, 1257 (1923).

<sup>16</sup> *J. Soc. Chem. Ind.*, 43, 35 T (1924).

of cc required by the sample is subtracted from the number of cc required by the blank. This difference  $\times .0024$  = the number of grams of furfural in 200 cc of the original distillate. Powell and Whittaker claim that the method when applied to various pulps and to sawdust compares favorably with the gravimetric phloroglucinol method.

An entirely satisfactory method for the determination of pentosans in wood should serve to differentiate sharply between furfural on the one hand and methyl- and hydroxymethylfurfural on the other. It should be specific for the pentosans and should not include other aldehyde-yielding substances in wood. Up to the present no such method has been devised.

### The Determination of Mannans

The most satisfactory method for determining mannans in wood is described by Schorger. It depends on the hydrolysis of mannans to mannose, which is then precipitated as the insoluble phenylhydrazone. Recent studies on the mannan determination by Heuser and Dammel<sup>17</sup> have established Schorger's method. It is questionable whether this method, without some modifications, can be applied when relatively small amounts of mannans are present in wood (as reported in the case of certain hardwoods).

Ten grams of the fine material with 150 cc of hydrochloric acid, specific gravity 1.025, are placed in an Erlenmeyer flask connected with a reflux condenser and boiled for three and one-half hours. The contents are then filtered into a 500 cc flask, and the sawdust washed back into the Erlenmeyer with about 100 cc of distilled water. The sawdust is then digested a short time over a Bunsen burner, and again filtered. This method of extraction is continued until the total filtrate amounts to 500 cc. The solution is then transferred to an 800 cc beaker, neutralized with 10 per cent NaOH, rendered slightly acid with acetic acid, and evaporated on the steam bath overnight to 150 cc. The solution is again filtered to remove humus matter, the filter being washed with a little cold water. A mixture of 10 cc of phenylhydrazine and 20 cc of water, rendered acid with glacial acetic acid, is added to the filtrate contained in a 200 cc Erlenmeyer. The flask (with frequent shaking) is allowed to stand 2 hours. The precipitate of mannose phenylhydrazone is collected in a weighed alundum or Gooch crucible, washed with cold water, then with acetone to remove resinous impurities, dried and weighed. The mannan content is calculated from the weight of the mannose phenylhydrazone by multiplying by the factor 0.6.

<sup>17</sup> *Cellulosechemic*, 5, 45 (1924).

### The Galactan Determination

The method used in determining the galactans in wood depends upon their hydrolysis to galactose and the oxidation of this sugar to mucic acid. The procedure which has been severely criticized and modified at various times<sup>18</sup> is still quite unreliable. Schorger made numerous experiments in the hope of improving the official method<sup>19</sup> but without much success, even when isolated galactans were used in the analysis.

Dore, using Schorger's modifications, describes the galactan method as follows:

Five grams of the material are placed in a 100 cc beaker, and 60 cc of nitric acid (specific gravity 1.15) are added. The beaker is placed in a water bath and the liquid evaporated to about 20 cc, care being taken not to allow the temperature of the water bath to exceed 87° C. The mixture is then diluted to about 75 cc with hot water, and filtered. The residual cellulose is washed until the filtrate comes through practically colorless. A total volume of about 250 cc is generally thus obtained. The filtrate and washings are evaporated on the water bath at 87° C. to a volume of about 10 cc. The residue is set aside for several days to allow the mucic acid to separate out. Large crystals (possibly oxalic acid) always form at first, then a day or two later fine flakes of mucic acid separate. At this point the mixture is stirred vigorously to facilitate the precipitation. About 24 hours after the mucic acid appears the mixture is diluted with 20 cc of cold water. The larger crystals redissolve, leaving the mucic acid unaffected. After a further 24 hours' standing the mucic acid is filtered off on a tared asbestos Gooch crucible and washed with about 50 cc of water, 60 cc of alcohol, and several times with ether. It is then dried at 100° for 3 hours and weighed. Galactan is calculated by multiplying the weight of the residue by the factor 1.2.

Dore points out that a critical study of the determination of galactan would be welcomed. While the method gives reasonably good results with *pure* galactose, it gives low and fluctuating results with galactans and results which, when applied to wood, are entirely unsatisfactory. With isolated galactan, Schorger was able to recover 28-65 per cent of the original material as mucic acid. Dore reports that by the use of the method a sample of redwood yielded 0.40 per cent and 0.47 per cent galactans (in duplicate determinations). An individual sample of yellow pine yielded 0.96 per cent, 0.66 per cent, 0.43 per cent and 0.80 per cent galactans. Apparently the method gives minimal values, which furnish

<sup>18</sup> Dore, *J. Ind. Eng. Chem.*, 7, 721 (1915); *ibid.*, 12, 476 (1920); Schorger, *ibid.*, 8, 494 (1916).

<sup>19</sup> Bur. Chemistry, U. S. Dept. Agric. Bull. 107, p. 55.

the analyst with little more than a rough idea of the approximate galactan content of the wood.

### Hemicellulose Determinations

The inherent difficulties in determining hemicelluloses in wood must be apparent from the discussion in Chapter 2, Part III, of this monograph. One of the most elaborate attempts to separate hemicelluloses quantitatively from "ortho" cellulose was made by Konig and Becker<sup>20</sup> but it is obvious that their method of analysis is purely arbitrary. Finely divided wood samples were treated with 0.4 per cent  $H_2SO_4$  under pressure. The temperature of the autoclave and the period of treatment varied with each species of wood examined, since it soon became evident that the rate of hydrolysis of the hemicelluloses varied in different wood samples.

In the case of hardwoods, 4-gram samples were hydrolyzed in autoclaves with 200 cc of 0.4 per cent  $H_2SO_4$ , the time periods and pressures varying with each sample. The undissolved residue was filtered off and washed. Its pentosan content was then determined. The filtrate and washings were neutralized with  $CaCO_3$ , evaporated and made up to a definite volume (200 cc). This solution was again filtered and aliquot portions taken for analysis. The total reducing sugar was determined by Meissel-Allihi's method in 20 cc of this filtrate. Another 100 cc portion was subjected to fermentation under standardized conditions at 30° C. after addition of Raulin's nutrient solution. Finally a separate 1-gram sample of wood was autoclaved with 100 cc of 0.4 per cent  $H_2SO_4$  and the residue filtered off on a Gooch crucible washed, dried and weighed. A pentosan determination was made on the filtrate.

In the case of coniferous woods, three 4-gram samples were autoclaved with 200 cc of 0.4 per cent  $H_2SO_4$ . Konig and Becker used a pressure of 2.5 atmospheres in the case of pine. The undissolved residues were filtered off and the total sugar, fermentable sugar, and soluble pentoses determined in the filtrates. Residual pentosans were determined in one residue after the autoclaving. The other two residues were again autoclaved with 200 cc of 0.4 per cent  $H_2SO_4$ . Again the residues were filtered off, the sugar determinations made on the filtrates and the pentosans determined in one of the two insoluble residues. The remaining residue was then resubjected to the same treatment and similar determinations made on the filtrate and final residue. While the first treatment removed most of the hydrolyzable hexosans and pentosans, Konig and Becker's figures show that the hydrolysis is not clean-cut but that the residue and insoluble pentosan content diminishes and the

<sup>20</sup> Z. angew. Chem., 32, 115 (1919); Papierfabrikant, 17, 982-7, 1014-19, 1171-4 (1919).

soluble hexosan and soluble pentosan contents of filtrates increase with successive hydrolyses.

To calculate the "hemicelluloses" (i.e., hydrolyzable hexosans and hydrolyzable pentosans) after such a determination, the total fermentable sugar of the filtrate is calculated as hexosans by multiplying by the factor 0.9. *The pentosan content of the insoluble residue* is then subtracted from the *total pentosan content of the original wood*. This gives a truer index of the *soluble pentosans* than does a direct determination in the filtrate due to inevitable losses of furfural in the acid solution. The sum of the total (non-cellulosic) hexosans and of the soluble pentosans equals the "hemicellulose content" of the wood.<sup>21</sup>

\* Further discussion of hemicelluloses and methods for their determination is beyond the province of this book. The reader is referred to the following bibliography: E. Schulze, *Ber.*, **24**, 2277 (1891), **22**, 1192 (1889); **23**, 2579 (1890); *Chem. Ztg.*, **19**, 1465 (1895); *Landw. Jahrb.*, **21**, 72 (1892); **23**, 1 (1894); *Zeits. physiol. Chem.*, **16**, 387 (1892); **19**, 38 (1894); **61**, 307 (1909); V. Graefe in Abderhalden's "Biochem. Handl." Vol. **2**, 42-60 (1911); Vol. **8**, 6-15 (1914); Czaplick, "Biochemie der Pflanzen," Vol. I, 647, 654 (1913). Tottingham, *et al.* *J. Biol. Chem.*, **45**, 407 (1921); *Ind. Eng. Chem.*, **16**, 139 (1924); Spoehr, *Publications Carnegie Inst., Washington*, No. 287, p. 79; Dore and Miller, *Univ. California Publications in Zoology*, **22**, No. 7, 389 (1923).

## Chapter 5

### The Determination of Lignin

As in the case of other proximate analytical procedures applied to wood, methods for the determination of lignin are quite arbitrary. Direct and indirect methods have been devised and besides these we have methods for the determination of certain substituent groups that are present in lignin.<sup>1</sup> None of these procedures is entirely satisfactory but they are all that we can expect after reviewing the present status of the chemistry of lignin.

#### **Direct Methods Used in Determining Lignin**

All direct methods for the determination of lignin depend upon its isolation from wood by means of an inorganic acid that will effect the solution of cellulose and other polysaccharides with the minimum attack on the residual lignin.

Probably the oldest and most commonly used method is due to Klason<sup>2</sup> although recent text books ascribe the procedure to Ost and Wilkening and to König.<sup>3</sup> Finely divided wood was treated with 70 per cent  $H_2SO_4$  at room temperature. The polysaccharides of wood dissolved to form a water-clear solution while the lignin remained insoluble. In applying the  $H_2SO_4$  method, König and his co-workers used 72 per cent acid and made their determination on wood that had been extracted with alcohol-benzol mixtures, followed by washing with alcohol and hot water. Dried 2-gram samples were thoroughly incorporated into 50 cc of 72 per cent  $H_2SO_4$  and the mixture was allowed to stand for about 48 hours. Five hundred cc of water were then added, the mixture brought to the boiling point and allowed to cool and to settle. The supernatant liquid was then decanted through a Gooch crucible and the lignin sediment filtered after being thoroughly washed by decantation. The filtrates no longer responded to the test for sulfates. The crucible and the lignin precipitate were dried at 105°, after which the lignin was ashed. The ash-free lignin content was then computed.

<sup>1</sup> A translation by C. J. West of a detailed résumé of the methods used in the determination of lignin by Emil Heuser is given in *Paper*, 27 (Feb 9, 1921), p. 24.

<sup>2</sup> "Bericht der Vereins der Papier u Zellstoffchemiker" (1908), pp. 52-3.

<sup>3</sup> Schwalbe-Sieber, "Chemische Betriebskontrolle in der Zellstoff Industrie," 110; Cross and Bevan, "Researches on Cellulose," 3, 39 (1905-10).

The above procedure in very slightly modified form was used by Mahood and Cable.<sup>4</sup> They allowed the 72 per cent  $H_2SO_4$  to act upon the sample for only 16 hours and then diluted the mixture to a concentration of 3 per cent acid. Thereupon, the solution was boiled under reflux for 2 hours and filtered on a tared alundum crucible. The method gave somewhat lower results than when this final heating was entirely omitted, but the yields of lignin were so consistent and reproducible that the procedure was adopted.

Quite recently, Klason<sup>5</sup> modified his former procedure by recommending the use of 64 per cent  $H_2SO_4$  in the isolation of lignin from wood. After standing for several days in a stoppered cylinder (with or without agitation of the mixture) the  $H_2SO_4$  is diluted with water and the lignin is filtered and washed until the filtrate is but faintly acid. The lignin precipitate is then washed with 50 cc of hot alcohol to remove rosin and fats. Five cc of 0.1 N KOH are then added to the precipitate and the washing with water is continued until the solution is no longer alkaline. The lignin precipitate is then dried at 105° C. and subsequently ashed. The ash (which contains some  $K_2SO_4$ ) is subtracted from the crude lignin content.

Klason and others have shown that lignin isolated with  $H_2SO_4$  always retains appreciable amounts of the acid. In fact the per cent of acid retained appears to increase with increasing concentrations of  $H_2SO_4$  used in the lignin determination. They have also shown that the acetyl groups which many chemists associate with the lignin<sup>6</sup> are split off by this treatment and that a part of the methoxyl content is also lost. We have here some partly compensating losses and gains in the determination. Besides these, some investigators believe that a portion of the extractives removed by certain non-aqueous solvents rightly belong with the lignin. von Euler<sup>7</sup> has attempted to apply certain corrections to the lignin determination (when 72 per cent  $H_2SO_4$  is used) and to arrive at *rational* lignin values in the case of coniferous woods. To correct for acetic acid split off from the lignin, the per cent crude lignin must be increased by 2 per cent. A further empirical correction of -- 5.7 per cent is made to account for the  $H_2SO_4$  which cannot be removed from isolated lignin by washing. To the resulting figure is added the per cent of alcoholic extractives (found after the wood has been extracted preliminarily with benzene) and this corrected value is termed the "true" or "*rational*" percentage of lignin. The following is an example of von Euler's procedure. An analysis of Norway spruce yielded 3.53 per cent of alcohol

<sup>4</sup>J. Ind. Eng. Chem., 14, 933 (1922)

<sup>5</sup>Cellulosechemie, 4, 82 (1923).

<sup>6</sup>Cf. Chapter 3, Part II

<sup>7</sup>Cellulosechemie, 4, 1 (1923).

soluble resins (*a*). The crude lignin (*b*) isolated by 72 per cent H<sub>2</sub>SO<sub>4</sub> was shown to be 30.5 per cent. Then the *rational* per cent lignin would be:

$$[(a) + (b)] + 2 \text{ per cent} - 5.7 \text{ per cent} = 30.3 \text{ per cent}$$

(acetic acid correction)	(adsorbed H <sub>2</sub> SO <sub>4</sub> correction)
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It should be noted that the corrections very nearly nullify each other and that the new value is very little different from the uncorrected value. In fact, von Euler's analytical data, in which she has applied these corrections, are little different from those of Klason.

Other corrections for the conversion of the lignin isolated by H<sub>2</sub>SO<sub>4</sub> into "true lignin" values have been proposed<sup>8</sup> but we do not propose to discuss them. The chemistry of lignin is as yet too insecure to warrant speculative excursions into the realm of "pure lignin."

The use of fuming HCl (*d* 1.21) in place of H<sub>2</sub>SO<sub>4</sub> in the isolation of lignin was proposed by Willstatter and Zechmeister<sup>9</sup> and this method has been adopted in the quantitative determination of lignin in a number of recent analytical investigations. Krull<sup>10</sup> has used the following procedure. One gram of wood meal that had been previously extracted with an alcohol-benzene mixture is transferred to a large, thick-walled test tube by means of 6 cc of water. The test tube is immersed in an ice bath and gaseous HCl is conducted into the suspension until there is no further change in the thin liquid which is then allowed to stand for 24 hours. At the end of this period a microscopic examination should show that no cellular structure is retained. The mixture is then diluted with water, filtered, and the lignin precipitate washed with hot water, dried, weighed and then ignited.

Dore<sup>11</sup> modified this procedure by moistening the extracted wood with 10 cc of concentrated (not fuming) HCl in a 1 x 10 inch test tube (provided with rubber stoppers, inlet and outlet tubes) and by treating the mixture with hydrochloric acid gas for 2 hours. Excessive heat was thus avoided and water cooling replaced the ice bath suggested by Krull. The tube was then left closed for 24 hours and the contents were later diluted, filtered on a Gooch crucible and washed. The residue was dried at 100° C. for 16 hours and then weighed in a glass stoppered weighing bottle.

In place of the highly concentrated HCl, a dilute acid solution may be used to saccharify the polysaccharides of wood, provided higher pres-

<sup>8</sup>von Fellenberg, *C. A.*, 11, 2122; Dore, *J. Ind. Eng. Chem.*, 11, 556 (1919).

<sup>9</sup>Ber., 46, 4201 (1913).

<sup>10</sup>Dissertation, Danzig (1916), "Versuche über Verzuckerung der Zellulose."

<sup>11</sup>*J. Ind. Eng. Chem.*, 12, 984 (1920).

sures may be resorted to. König and Rump<sup>12</sup> heat wood with 1-2 per cent HCl under 6 atmospheres pressure to remove polysaccharides, in determining the percentage lignin. König and Becker<sup>13</sup> have made a comparative study of different acid methods used in the analysis of lignin. Their results are reproduced in Table XVI. The data show that there is a surprisingly good agreement between the results obtained by the various methods. Only in the case of the analysis of birch and ash are the results obtained by the H<sub>2</sub>SO<sub>4</sub> method markedly lowered.

TABLE XVI  
PERCENTAGE OF LIGNIN OBTAINED BY DIFFERENT METHODS OF ISOLATION  
(KÖNIG AND BECKER)

Wood Used	Heating Under Pressure with		72 Per Cent H <sub>2</sub> SO <sub>4</sub>	HCl d. 1.21
	1 Per Cent HCl	Gaseous HCl		
1. Fir . . . . .	29.94	28.81	29.36	29.17
2. Fir . . . . .	28.91	28.10	28.04	27.98
3. Pine . . . . .	29.52	29.56	31.33	29.16
4. Birch . . . . .	23.54	22.55	20.96	23.27
5. Birch . . . . .	27.28	26.36	26.75	26.38
6. Poplar . . . . .	22.14	22.36	22.06	22.45
7. Poplar . . . . .	21.00	21.06	21.91	20.75
8. Beech . . . . .	22.07	22.90	23.99	22.69
9. Ash . . . . .	26.71	25.90	19.59	26.01
10. Willow . . . . .	25.06	25.97	24.54	24.70
11. Alder . . . . .	25.95	23.04	23.05	24.57

Various modifications of the acid methods for lignin isolation have been suggested.<sup>14</sup> One of the most recent ones is that of H. Schwalbe,<sup>15</sup> who moistens extracted wood with HCl (d 1.07) and then treats the mixture with 72 per cent H<sub>2</sub>SO<sub>4</sub>. Gelatinization of the wood, which is an objectionable feature of the analysis, is prevented. On the other hand, Schwalbe's results are so much lower than those obtained by the older methods that his procedure must be closely scrutinized before it can be accepted.

#### Indirect Methods Used in Determining Lignin

These methods depend, either on (1) the determination of the non-lignin components of the wood with subsequent calculation of lignin "by difference," or (2) on the determination of fission products or proximate groups of the lignin.

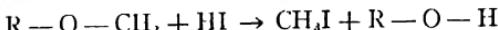
Detailed reference has been made to the isolation of skeletal substances of wood by the  $\text{ClO}_2$ — $\text{Na}_2\text{SO}_3$  method of Schmidt and his co-workers.<sup>16</sup> Since his reagents do not attack isolated cellulose, mannan, xyloans, or the common sugars, Schmidt advances the viewpoint that any materials of the nature of polysaccharides that are removed by the  $\text{ClO}_2$  treatment must be classed with lignin. These findings have been vigorously disputed.<sup>17</sup> Here again we come face to face with the difficult, seemingly insoluble, problem of determining whether certain carbohydrates belong properly with cellulose or with lignin or whether they form a separate group of components in wood.

If we should concede that only the encrusting materials are attacked by the  $\text{ClO}_2$  procedure, then the lignin content of wood could be determined by simply subtracting the per cent of "skeletal substances" from 100. When this is done, however, "lignin" yields ranging from 37-46 per cent are obtained and these yields are much higher than those found by the use of any direct method for the determination of lignin. Heuser and Merlau have shown that if due correction is made for the per cent carbohydrates that are leached out (and reckoned with the "lignin") when Schmidt's method is employed, lignin figures are obtained that are consistent with those found by other methods. For example, by Schmidt's method a spruce wood yielded 62.7 per cent "skeletal substances." This would indicate a lignin content of 37.3 per cent. However, the carbohydrates ("hemicelluloses") lost during the Schmidt treatment totalled 7.3 per cent. If these are taken into account, the corrected lignin figure is lowered to 30 per cent which is quite comparable with other spruce lignin data.

### The Methoxyl Determination

Since methoxy ( $\text{CH}_3-\text{O}-$ ) groups are always associated with lignin, the determination of *methoxyl* in wood has received a good deal of attention. In fact, attempts have been made (without marked success) to use the methoxyl content of wood in calculating the percentage lignin.

When compounds containing the methoxyl group are treated with hydriodic acid, the methyl group is removed as methyl iodide:



When the volatile alkyl iodide is passed into alcoholic silver nitrate solution it is decomposed quantitatively into silver iodide which may be determined by the usual methods. The method is due to Zeisel<sup>18</sup> and was applied by Benedict and Bamberger to the determination of methoxyl

groups in plant tissues.<sup>19</sup> Numerous pieces of apparatus have been devised for carrying out the methoxyl determination and numerous modifications in the original method have been suggested. These are discussed comprehensively by Hans Meyer.<sup>20</sup> The ground-in glass equipment designed by Stritar is recommended and described by Schwalbe and Sieber.<sup>21</sup> Dore<sup>22</sup> has used the following simplified procedure which has given him consistent results in the analysis of woods. The decomposition flask to which the sample was added was a small distillation flask (of 130 cc capacity) having its side arm connected with a CO<sub>2</sub> generator. In the mouth of the flask was placed a perforated cork with a delivery tube which ran vertically upwards for 50 cm and acted in part as a reflux condenser and fractionating column. The delivery tube was then bent twice at right angles and descending was joined at its lower extremity with two U-tubes, themselves connected in series. The first of these U-tubes contained distilled water and a few milligrams of red phosphorus. The second contained only distilled water. The U-tubes were so arranged that they could be placed in a beaker of water that could be heated with a bunsen burner. From the second U-tube a delivery tube ran to the absorption apparatus which consisted of an Erlenmeyer flask and a Fresenius nitrogen bulb. The arrangement is shown in the accompanying sketch (from which the heating bath and CO<sub>2</sub> generator are omitted).

In the first and second absorption flasks were placed 35 and 15 cc, respectively, of freshly filtered alcoholic silver nitrate solution. (The solution was prepared by dissolving 10 grams of solid silver nitrate in 25 cc of water and adding 225 cc of 95 per cent alcohol.) 0.3 gram of material was placed in the decomposition flask and 15 cc of hydriodic acid (1.70 specific gravity) were added. The mixture was heated to 130° C. in a paraffin bath and the temperature maintained at 130° to 140° C., while a slow stream of carbon dioxide was passed through the apparatus. The beaker of water surrounding the U-tubes was kept at a temperature of 50° to 60° C. throughout the process. The operation was continued until the precipitated silver iodide in the absorption apparatus settled out, leaving a clear supernatant liquid, indicating the completion of the reaction.

The apparatus was then disconnected and the contents of the absorption flasks rinsed into a 600 cc beaker. Sufficient water to bring the volume to about 500 cc was added and the whole evaporated on the

<sup>19</sup> *Monatsh.*, 15, 509 (1894).

<sup>20</sup> "Analyse ii Konstitutions-ermittlung organischer Verbindungen," 1916, pp 739-751.

<sup>21</sup> "Betriebskontrolle," 2nd edition, p. 103.

<sup>22</sup> *J. Ind. Eng. Chem.*, 12, 472 (1920).

steam bath to a volume of 150 to 200 cc in order to expel the alcohol. A few drops of nitric acid were added, the solution again diluted to about 500 cc and allowed to stand on the steam bath for about one-half hour, thus allowing the silver iodide to settle. The precipitate was then collected in a tared asbestos Gooch crucible, washed, dried at 130° C. for 2 hours and weighed.  $\text{CH}_3\text{O}$  was calculated from the weight of silver iodide by multiplying by the factor 0.132.

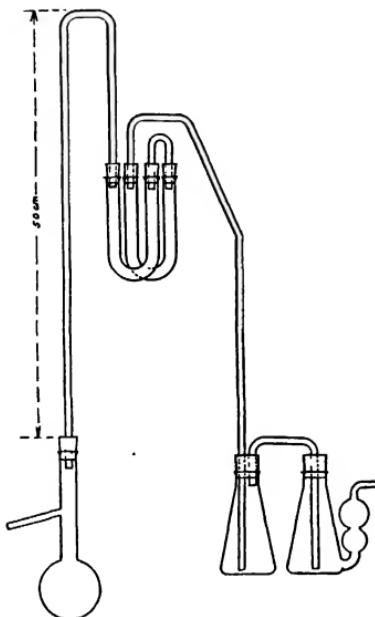


FIG. 8—Zeisel Apparatus used by Dore.

Schorger<sup>23</sup> has suggested that if many methoxyl determinations are to be made, a definite volume of standardized 0.1 N alcoholic  $\text{AgNO}_3$  may be used in the absorption apparatus. After the  $\text{AgI}$  has been filtered off the remaining  $\text{AgNO}_3$  may be titrated with standard KCNS solution, using ferric alum as indicator. One cc of 0.1 N  $\text{AgNO}_3$  = 0.0031 gram  $\text{CH}_3\text{O}$ . The particular type of Zeisel apparatus used by the U. S. Forest Products Laboratory for the determination of the

<sup>23</sup> *J. Ind. Eng. Chem.*, **9**, 556 (1917).

<sup>24</sup> *Ibid.*, **9**, 465 (1917).

methoxyl group has been briefly described by Pieper, Acree, and Humphrey.<sup>24</sup> It is illustrated in Figure 9. The connections are all made by means of ground-in glass joints and special absorption flasks are used. Rubber and cork stoppers are thus obviated.

Analytical investigations have indicated that the methoxyl contents of hardwoods is usually higher than that of softwoods. Ritter<sup>25</sup> has shown, however, that when lignin is isolated from wood by means of an acid, a larger proportion of the total methoxyl is recovered in the lignin of softwoods than in hardwood lignin. Ritter's results are given in Table

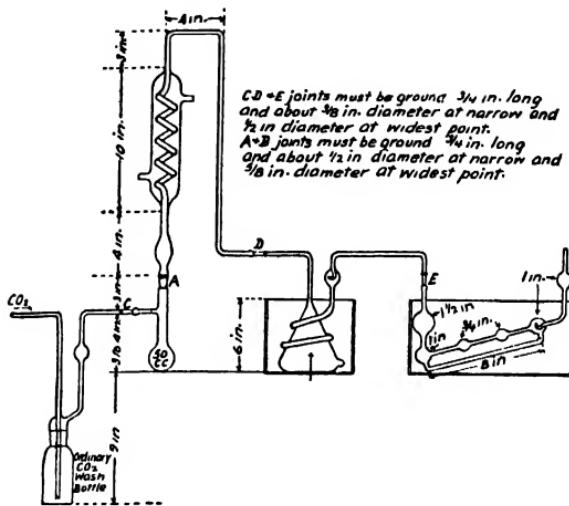


FIG 9—Zeisel Apparatus for Determining  $\text{CH}_3\text{O}$  Group.

XVII. Not only do they show certain analytical differences between the lignins but they indicate clearly that we cannot multiply the methoxyl content by one definite factor and thus calculate the lignin content of any wood. Such factors (if they could be used) for softwoods would often range from 5 to 6, while in the hardwoods they would seldom exceed 4. We have no experimental evidence that all lignins contain identical amounts of methoxyl. On the other hand, Ritter has shown quite recently that even in the same wood the lignin of the middle lamella contains a much higher proportion of the methoxyl groups than does the lignin found in the remainder of the cell wall.

<sup>24</sup> *Ind. Eng. Chem.*, 15, 1264 (1923).

TABLE XVII  
RELATION OF METHOXYL AND LIGNIN IN WOODS (AS REPORTED BY RITTER)

Species	Per Cent Lignin in Wood	Per Cent Cl <sub>2</sub> O in Wood	Per Cent CH <sub>3</sub> O X 100	Per Cent CH <sub>3</sub> O in Lignin	Per Cent CH <sub>3</sub> O Not Recovered in Isolated Lignin
	(1)	(2)	(3)	(4)	(5)
Western yellow pine . . .	26.75	4.45	16.64	13.13	3.51
Western white pine . . .	24.30	4.47	18.40	15.10	3.30
Incense cedar . . . . .	37.68	6.09	16.16	14.51	1.65
Mesquite . . . . .	30.77	5.49	17.84	14.05	3.79
Tan oak . . . . .	24.68	5.70	22.06	16.99	5.07
Eucalyptus . . . . .	26.74	6.56	24.53	15.01	9.52
Yellow poplar (sapwood)	23.86	5.89	24.69	17.00	7.69
Yellow poplar (heartwood)	23.69	6.03	25.45	20.22	5.23
Pignut hickory (heartwood)	22.85	5.79	25.34	18.43	6.91

### The Chlorine Number

Attempts have been made to gauge the degree of lignification by determining the weight of chlorine that will be taken up by a definite weight of wood. This method was devised by Waentig and his co-workers.<sup>26</sup> In a specially devised apparatus, provided with a CaCl<sub>2</sub> tube to prevent loss of water, moist wood is treated with a stream of dry chlorine until no further increase in weight is noted. The excess of chlorine is then replaced by dry air. The weight of chlorine taken up divided by the weight of dry, resin-free wood is termed the *chlorine number*. This number multiplied by 0.71 gives approximately the per cent of lignin in the wood.

### Other Indirect Methods for Determining Lignin

A number of other methods for indirectly judging the approximate amount of lignin in wood or wood pulps have been suggested. All of them leave much to be desired and a discussion of these methods lies beyond our province. Among them are the phloroglucinol absorption method of Cross, Bevan, and Briggs,<sup>27</sup> and the nitric acid reduction method of Seidel.<sup>28</sup> If we assume that all the acetic acid freed from wood by the action of dilute H<sub>2</sub>SO<sub>4</sub> is due to acetyl groups in lignin (a very hazardous assumption), we might include among the indirect methods for estimating lignin the "acid hydrolysis" devised by Schorger. This method has been described in a previous chapter (Miscellaneous Determinations) where it more logically belongs.

<sup>26</sup> Z. angew. Chem., 32, No. 44, 173 (1919).

<sup>27</sup> Ber., 40, 3119 (1907).

<sup>28</sup> Dissertation, Dresden, 1907.

It would appear that until chemists, plant physiologists, and wood technologists can concur on what the term *lignin* should include, analytical procedures for lignin must remain as empirical and as arbitrary as we find them today, and before this harmony can be established, a number of problems remain to be solved. Physical and organic chemists must find new means of attacking these problems of lignification before the analytical chemist can make much progress. Is lignin aromatic (Klason) or hydroaromatic (Strupp)? Should it be classed with the polysaccharides (Schmidt, Willstatter, Pringsheim)? Do all these classes figure in its composition? Is it composed largely of a few homogeneous substances or is it the sum total of all non-cellulosic substances (Wislicenus)? Is there one class of substances common to the lignin of all woods (Powell, Whittaker)? Do the pentosans belong in part with lignin or are they present in the nature of impurities? Do the acetyl groups belong properly with lignin? All these questions and many more are in dispute and their answers must antedate further analytical progress. Meanwhile, it is well to understand the impossibility of determining quantitatively something which we cannot clearly define in fundamental terms. While definitions based on proximate analytical procedures may prove extremely useful, they are always in danger of becoming fixed and inelastic and of obstructing future progressive research.

## Chapter 6

# Analytical Data and Their Significance

### The Practical Value of Wood Analyses

The limitations of various methods of analysis used in the examination of wood have been stressed in previous chapters. Their scientific and practical value deserves brief discussion at this point.

Not infrequently complete chemical analyses of wood are asked for when some simple practical test, or one or two specific determinations, would yield all the information required. Complete wood analyses seldom give specific information regarding the physical utilization of any wood. Their greatest merit lies in the fact that they yield comparative data (provided a standardized procedure has been used) that can be used statistically or in the interpretation of biological phenomena.

In this way they have furnished valuable information on the gradual destruction of certain wood components and the accumulation of others during wood decay. They have also indicated the changes wrought in wood after passage through the intestinal tract of the marine borer (*toredo*). Comparative analyses of wood before and after attack of termites (white ants) have also been made.<sup>1</sup> The analysis of wood destroyed by various insects would probably furnish valuable data to the entomologist. Similarly comparative wood analyses may prove of future benefit to the ecologist and the silviculturist. Many of these liaisons between the forest chemist and other branches of science are still in embryo or entirely untried.

Wood analyses have also permitted certain conclusions regarding the gradual conversion of wood into coal and have thrown a new light on the mechanism of coal formation. To give a concrete instance a brown lignite (the Japanese "umoregi") derived from a species of sequoia was examined by Komatsu and Ueda.<sup>2</sup> They found that the change from wood to *umoregi* had caused the loss of 20 per cent of the cellulose and an accumulation of lignin of about 25 per cent. Their results were based on the comparative analytical data obtained with a native redwood. Such analytical data, coupled with purely organic chemical studies on lignin,

<sup>1</sup>Cf. Chapter 2, Part V.

<sup>2</sup>Mem. Col. Sci. Kyoto, Imp. Univ. A. 7, 7 (1923)

have led one group of chemists at least to conclude that coal finds its precursor in the lignin, rather than in the cellulose of woody tissue.

Specific analytical determinations may also have a certain value. The Cross and Bevan cellulose determination shows the maximum amount of insoluble delignified material that could conceivably be obtained in any well conducted chemical pulping operation.<sup>3</sup> We hasten to add, however, that the amounts of pulp actually obtained in any such cook would (probably) never reach the limiting value set by Cross and Bevan's method and that purely analytical data can never be used in lieu of an experimental cook in judging the value of the raw material used for pulp making.

The determination of the resistant  $\alpha$ -cellulose in pulp may have practical importance in determining the value of such material in the manufacture of *rayon* (artificial silks), hydrated cellulose films (like cellophane), or in any plant operation in which chemical wood pulp is treated with alkali.

The extraneous components of wood are often of such great commercial interest that the determination of extractives becomes an important matter. A wood high in ether-soluble matter usually contains large amounts of resin (e.g., the lightwood of Southern pine). A large percentage of water-soluble material might give a clue or indication of a high percentage of tannins, coloring matter (or its precursors) or even of valuable water soluble carbohydrates (e.g., the galactans of Western larch). The determination of water-soluble or alkali-soluble extractives may also be of decided value in determining whether or not a wood should be used in the manufacture of various types of storage tanks. The identification and determination of volatile oils in certain oleoresins would probably orientate the entomologist in studying the attraction of certain trees for certain insects and the immunity of some woods to insect attack.

The determination of the methoxyl content of wood is also of some interest to the wood distiller. Here, however, a direct correlation of the methoxyl content with the amount of methanol obtained in wood distillation is hardly possible. The methoxyl content gives the wood distillation industry a mark at which to shoot, but which is never reached in practice.<sup>4</sup>

It should be borne in mind that special analyses may be devised (in place of tedious systematic schemes of analysis) to answer specific practical questions put to the chemist. As an example, a determination of the intensity of acidity of water extracts of different woods that are used out of doors and which make contact with metal fittings or which are placed near metal gutters might serve in determining which woods cause the least corrosion.

<sup>3</sup>Cf. Chapter 4, Part IV.

<sup>4</sup>Cf. Chapter 2, Part IV.

### Earlier Analytical Data

Data compiled by earlier wood analysts need not be reproduced. Schwalbe<sup>5</sup> cites the work of Franz Schulze and Lange, who determined cellulose in several woods by means of the chlorate method.<sup>6</sup> The average cellulose content was about 50 per cent of the dry weight of the wood. Hugo Muller<sup>7</sup> used the bromine-water method for determining cellulose. His results are given in Table XVIII. These form a summative analysis of wood, in which the "encrusting substances" include all the non-cellulose material not included under *water extractives* and *resins*, and which are, therefore, not comparable with the usual lignin determinations. Dean and Tower, applying the Cross and Bevan cellulose method to wood, obtained results which averaged about 53 per cent.<sup>8</sup> Other chemists, however, have reported much higher cellulose contents, often exceeding 60 per cent.

TABLE XVIII  
ANALYSIS OF WOODS BY HUGO MULLER (BROMINE METHOD FOR CELLULOSE)  
(Results given on air dried samples)

Wood	Per Cent $H_2O$	Per Cent Water-Soluble Material	Per Cent Resin	Per Cent Cellulose	Per Cent Encrusting Substances
Birch . . . . .	12.48	2.65	1.14	55.52	28.21
Beech . . . . .	12.57	2.41	0.41	45.47	39.14
Boxwood . . . . .	12.90	2.63	0.63	48.14	35.70
Ebony . . . . .	9.40	9.99	2.54	29.99	48.08
Oak . . . . .	13.12	12.20	0.91	39.47	34.30
Alder . . . . .	10.70	2.48	0.87	54.62	31.33
Guaiac . . . . .	10.88	6.06	15.63	32.22	35.21
Basswood . . . . .	10.10	3.56	3.93	53.09	29.32
Chestnut . . . . .	12.03	5.41	1.10	52.64	28.82
Pine . . . . .	12.87	4.05	1.63	53.27	28.18
Mahogany . . . . .	12.39	9.91	1.02	49.07	27.61
Poplar . . . . .	12.10	2.88	1.37	62.77	20.88
Fir . . . . .	13.87	1.26	0.97	56.99	26.91
Teak . . . . .	11.05	3.93	3.74	43.12	38.16
Willow . . . . .	11.66	2.65	1.23	55.72	28.74

### Proximate Analyses Data Obtained on Hardwoods and Softwoods

Table XIX gives a résumé of proximate analyses of American woods carried out at the Forest Products Laboratory between 1917-1922. It will be noted that in general, the sum of the lignin, cellulose and alkali-soluble fractions accounts for the greater part of the dry wood (96-105 per cent of the total weight).

<sup>5</sup>"Chemie der Cellulose," p. 440.

<sup>6</sup>*Zeits. physiol. Chem.*, 14, 15 and 283 (1889).

<sup>7</sup>"Pflanzenfaser," p 150, cited by Schwalbe.

<sup>8</sup>*J. Am. Chem. Soc.*, 29, 1119 (1907).

TABLE  
PROXIMATE ANALYSES OF WOODS (MEAN VALUES  
(Results in percentage of

Species	Ash	Solubility in			1 Per Cent NaOH	Acetic Acid
		Cold Water	Hot Water	Ether		
Western yellow pine ( <i>Pinus ponderosa</i> ) .....	0.46	4.09	5.05	8.52	20.30	1.09
Yellow cedar ( <i>Chamaecyparis nootkatensis</i> ) .....	0.43	2.47	3.11	2.55	13.41	1.59
Incense cedar ( <i>Libocedrus decurrens</i> ) .....	0.34	3.64	5.38	4.31	17.69	0.91
Redwood (heartwood) ( <i>Sequoia sempervirens</i> ) .....	0.21	7.36	9.86	1.07	20.00	1.08
Western white pine ( <i>Pinus monticola</i> ) .....	0.20	3.16	4.49	4.26	14.78	1.03
Longleaf pine ( <i>Pinus palustris</i> ) .....	0.37	6.20	7.15	6.32	22.36	0.76
Douglas fir ( <i>Pseudotsuga taxifolia</i> ) .....	0.38	3.54	6.50	1.02	16.11	1.04
Western larch ( <i>Larix occidentalis</i> ) .....	0.23	10.61	12.59	0.81	22.14	0.71
White spruce ( <i>Picea canadensis</i> ) .....	0.31	1.12	2.14	1.36	11.57	1.59
Tanbark oak ( <i>Quercus densiflora</i> ) .....	0.83	4.10	5.60	0.80	23.96	5.23
Mesquite ( <i>Prosopis juliflora</i> ) .....	0.54	12.62	15.09	2.30	28.52	2.03
Balsa ( <i>Ochroma lagopus</i> ) .....	2.12	1.77	2.79	1.23	20.37	5.80
Hickory (shelbark) ( <i>Illicoria ovata</i> ) .....	0.69	4.78	5.57	0.63	19.04	2.51
Eucalyptus ( <i>Eucalyptus globulus</i> ) .....	0.24	4.67	6.98	0.56	18.57	1.85
Basswood ( <i>Tilia americana</i> ) .....	0.86	2.12	4.07	1.96	23.76	5.79
Yellow birch ( <i>Betula lutea</i> ) .....	0.52	2.67	3.97	0.60	19.85	4.30
Sugar maple ( <i>Acer saccharum</i> ) .....	0.44	2.65	4.36	0.25	17.64	4.46

Usually hardwoods give a higher yield of volatile acid on hydrolysis than do the softwoods and the pentosan content of hardwoods is roughly twice that of the conifers. While softwoods in general show a higher methylpentosan content than do the hardwoods, the determination is of such questionable value that general conclusions are unwarranted. The methoxyl content of softwoods is appreciably lower than that of hardwoods.

The Cross and Bevan celluloses isolated from both soft- and hardwoods retain between 40 and 65 per cent of the furfural-yielding substances of the original wood. The hardwood "cellulose fraction" usually retains somewhat more of the pentosans originally present in the wood than do cellulose fractions isolated from the softwoods. This means that Cross and Bevan hardwood cellulose often retains two and one-half times as much pentosans as the Cross and Bevan cellulose obtained from conifers.

## XIX

OBTAINED BY THE U. S. FOREST PRODUCTS LABORATORY  
oven-dry (105° C.) samples

Meth- oxy	Pento- san	Methyl pento- san	Cellu- lose	Lignin	Pento- san	In Cellulose			
						Methyl pento- san	$\alpha$ - Cellu- lose	$\beta$ - Cellu- lose	$\gamma$ - Cellu- lose
4.49	7.35	1.62	57.41	26.65	6.82	1.98	62.10	10.56	30.13
5.25	7.87	3.42	53.86	31.32	7.30	1.78	62.68	11.06	26.25
6.24	10.65	1.35	41.60	37.68	9.08	1.99	46.92	11.67	41.06
5.21	7.80	2.75	48.45	34.21	7.40	2.09	78.81	2.95	18.24
4.56	6.97	3.22	59.71	26.44	5.33	1.95	64.61	16.32	19.06
5.05	7.46	3.60	58.48	—	7.71	1.16	—	—	—
4.95	6.02	4.41	61.47	—	5.34	1.20	—	—	—
5.03	10.80	2.81	57.80	—	8.94	1.19	—	—	—
5.30	10.39	3.55	61.85	—	9.63	0.72	—	—	—
5.74	19.59	—	58.03	24.85	22.82	—	56.77	19.92	23.03
5.55	13.96	0.70	45.48	30.47	17.75	0.81	76.48	2.35	21.17
5.68	17.65	0.86	54.15	26.50	19.99	1.35	75.64	0.27	24.08
5.63	18.82	0.80	56.22	23.44	21.89	1.41	76.32	2.82	20.35
6.73	20.09	2.33	57.62	25.07	20.96	2.46	68.86	0.70	31.10
6.00	19.93	3.73	61.24	—	24.28	1.54	—	—	—
6.07	24.63	2.69	61.31	—	28.30	1.16	—	—	—
7.25	21.71	2.39	60.78	—	24.48	0.96	—	—	—

If due correction is made for these furfural-yielding substances in the Cross and Bevan cellulose, the "pentosan-free cellulose" figures are generally higher in the case of conifers than in the hardwoods. The danger of generalizing, however, is shown by studying the analysis of incense cedar which gives extraordinarily high figures for lignin (nearly 38 per cent) and correspondingly low yields of Cross and Bevan cellulose. The "pentosan-corrected" cellulose values for incense-cedar then approximate 37 per cent, a figure which approaches the figures found in mesquite, a hardwood very low in cellulose.

#### Analytical Differences in Heart- and Sapwood

Table XX gives a résumé of data obtained by applying the proximate methods of the Forest Products Laboratory to heartwood and sapwood

TABLE  
ANALYSES OF SAPWOOD AND HEARTWOOD OF SOME  
(Results in percentage of)

Species	Ash	Solubility in			1 Per Cent NaOH	Acetic Acid	Meth- oxyl
		Cold Water	Hot Water	Ether			
White ash:							
No. 2 sapwood . . .	0.61	5.81	6.41	1.17	21.77	3.23	4.70
No. 2 heartwood . . .	0.30	2.24	3.40	0.43	19.59	2.31	5.36
No. 3 sapwood . . . .	0.57	5.25	7.02	0.88	21.93	3.70	5.66
No. 3 heartwood . . . .	0.32	2.12	4.46	0.46	18.97	2.66	5.20
Yellow poplar.							
No. 1 sapwood . . . .	0.48	1.29	1.98	0.27	16.74	3.12	5.81
No. 1 heartwood . . . .	0.39	1.50	2.08	0.43	17.70	2.89	5.86
No. 2 sapwood . . . .	0.36	1.45	2.51	0.13	16.91	3.33	5.89
No. 2 heartwood . . . .	0.33	1.45	2.89	0.58	17.57	2.73	6.03
Pignut hickory.							
No. 1 sapwood . . . .	0.40	4.91	6.45	0.29	19.11	3.58	5.56
No. 2 heartwood . . . .	0.45	2.07	2.95	0.36	15.10	3.08	5.79
Yellow birch.							
No. 1 sapwood . . . .	0.26	1.05	1.98	0.48	16.77	2.34	5.66
No. 1 heartwood . . . .	0.40	4.16	5.69	0.81	20.51	1.78	5.46
No. 2 sapwood . . . .	0.18	1.74	2.10	0.88	19.78	3.75	5.47
No. 2 heartwood . . . .	0.23	2.76	3.96	0.99	21.14	2.83	5.27
White oak.							
No. 1 sapwood . . . .	0.57	2.55	4.11	0.46	21.11	3.44	5.95
No. 1 heartwood . . . .	0.43	7.33	10.15	0.71	25.81	2.59	6.18
No. 2 sapwood . . . .	0.37	4.27	5.73	0.65	21.69	2.47	6.02
No. 2 heartwood . . . .	0.42	4.76	6.60	0.62	22.67	2.97	5.64
Bald cypress:							
No. 1 sapwood . . . .	0.48	0.72	1.42	0.23	8.55	0.77	4.35
No. 1 heartwood . . . .	0.30	2.79	2.99	4.87	10.59	0.48	3.94
No. 2 sapwood . . . .	0.86	1.76	2.30	2.80	10.63	0.65	4.99
No. 2 heartwood . . . .	0.95	3.27	3.49	7.93	13.56	0.29	4.07
White pine:							
No. 1 sapwood . . . .	0.23	3.55	5.15	5.46	17.16	1.68	4.16
No. 1 heartwood . . . .	0.42	5.97	7.68	3.62	19.15	1.43	4.60
Yellow cedar:							
No. 1 sapwood . . . .	0.28	2.13	3.41	1.00	11.72	2.05	4.40
No. 1 heartwood . . . .	0.18	2.88	4.12	1.32	12.77	1.53	4.81
White cedar:							
No. 2 sapwood . . . .	0.64	2.18	2.82	—	11.02	1.17	5.07
No. 2 heartwood . . . .	0.21	1.94	3.22	—	11.41	0.84	5.00
No. 3 sapwood . . . .	0.48	3.02	3.96	1.44	12.71	1.11	5.23
No. 3 heartwood . . . .	0.27	2.80	4.01	1.87	14.14	0.74	5.09
Incense cedar:							
No. 1 sapwood . . . .	0.47	1.92	2.97	0.67	11.16	1.33	5.95
No. 1 heartwood . . . .	0.30	4.74	7.08	4.78	19.99	0.68	6.21

of different species. Ritter and Fleck<sup>8</sup> have found that in the case of softwoods, the water, ether, and alkali-soluble components are higher in heartwood than in sapwood and that (with the exception of lignin of white cedar) the cellulose and lignin are lower in the heartwood. It

<sup>8</sup>Ind Eng Chem, 15, 1056 (1923).

## XX

AMERICAN WOODS (BY RITTER AND FLECK)  
oven-dry (105° C.) samples

Pento-san	Méthyl pento-san	Cellu-lo-se	Lig-nin	Pento-san	Méthyl pento-san	In Cellulose		
						Alpha	Beta	Gamma
19.85	2.40	50.38	26.95	18.83	1.60	74.67	13.67	11.66
19.90	2.25	53.56	27.39	16.75	1.34	64.68	24.58	10.84
20.16	2.63	49.72	27.39	19.67	1.60	55.11	28.29	16.50
19.87	2.46	53.40	28.38 *	17.34	1.47	42.45	33.22	24.33
18.37	3.28	58.13	23.08	15.52	2.21	50.13	30.74	19.13
18.47	3.11	59.57	22.19	14.97	2.40	61.30	20.20	18.50
18.82	1.22	58.02	23.86	19.01	0.78	34.32	48.52	17.16
19.08	1.13	59.47	23.69	17.83	1.47	36.67	42.75	20.58
18.18	1.11	56.08	21.87	16.90	1.30	51.55	21.92	26.53
18.64	1.02	58.81	22.85	16.20	1.39	59.44	23.74	16.82
21.36	1.66	58.91	24.69	20.72	1.13	52.15	32.90	14.45
20.37	1.39	56.88	24.62	21.87	1.12	61.17	23.23	15.60
22.30	1.82	56.57	27.76	22.19	1.71	52.40	26.82	20.78
23.21	1.07	54.93	28.13	21.81	1.04	53.56	25.00	21.44
23.25	0.90	49.53	32.34	24.74	0.88	68.07	15.27	16.66
21.82	1.57	48.68	32.74	24.22	0.58	67.33	11.84	20.83
21.72	0.94	53.18	31.14	24.81	1.20	53.81	22.63	23.56
22.08	0.91	52.12	31.30	24.54	0.96	52.96	20.41	26.63
8.03	4.38	54.86	35.01	6.25	1.85	76.09	5.93	17.98
6.67	4.49	53.10	33.06	5.84	1.80	76.83	3.94	19.23
9.23	3.34	50.94	35.31	5.89	1.65	58.18	26.91	14.91
7.88	3.36	49.18	32.27	6.33	1.25	57.38	24.75	17.87
9.31	2.14	54.25	26.51	6.81	2.09	54.56	17.47	27.97
8.56	1.00	50.23	26.14	7.12	2.02	57.29	22.42	19.29
8.47	1.75	58.12	29.03	7.60	2.44	54.61	26.59	18.80
8.69	1.85	56.08	28.73	7.78	2.73	—	20.17	—
11.61	0.94	55.77	29.85	10.35	1.77	73.78	0.99	25.23
10.79	1.72	55.19	31.39	8.52	1.58	61.47	22.23	16.30
10.82	1.16	55.02	32.14	8.95	1.28	69.17	14.04	16.79
10.36	1.56	54.42	32.42	7.97	1.32	55.22	24.74	20.04
12.08	0.45	49.09	34.73	10.14	1.24	50.69	12.98	36.33
12.04	0.56	44.53	33.67	11.68	1.31	66.62	11.05	22.33

is more difficult to generalize in the case of hardwoods. Certain hardwoods (like oak) show a higher per cent extractives in the heartwood than in the sapwood. These same hardwoods show a lower cellulose content in the heartwood than in the sapwood. Other hardwoods (like pignut hickory) show a higher per cent extractives in the sapwood than in

TABLE XXI  
ANALYSES OF SPRINGWOOD AND SUMMERWOOD OF SOME AMERICAN Woods  
(Results in percentages on oven-dry (105° C.) samples)  
(Rutter and Fleck)

Species		Solubility in			Acetic Acid	Methoxy	Pento-sans	Lignin	Cellulose	Pento-sans in Cellulose
		Cold Water	Hot Water	1 Per Cent NaOH						
Douglas fir										
Hearwood	Springwood .....	3.00	4.67	15.10	0.62	3.48	11.97	32.61	55.95	8.31
	Summerwood .....	2.15	3.76	14.56	0.71	3.40	9.89	29.20	59.35	6.50
Western white pine										
Heartwood	Springwood .....	3.76	5.16	22.08	1.42	3.68	10.07	26.30	57.60	7.27
	Summerwood .....	4.29	5.42	21.47	1.40	3.85	9.82	25.30	60.00	6.94
Loblolly pine										
Sapwood	Springwood .....	3.28	3.49	11.11	1.28	4.05	11.59	28.12	58.06	8.78
	Summerwood .....	2.18	2.97	11.01	1.41	4.18	11.12	26.78	61.21	8.69
Heartwood	Springwood .....	7.50	7.16	18.14	1.00	6.17	12.77	26.78	53.44	11.52
	Summerwood .....	7.64	6.44	21.19	1.11	6.88	12.12	24.18	52.87	11.20
Catalpa										
Sapwood	Springwood .....	9.12	12.44	34.45	3.33	4.44	22.39	23.64	50.37	25.94
	Summerwood .....	7.29	10.11	27.97	4.45	4.10	22.35	18.68	56.49	22.09
Heartwood	Springwood .....	7.51	11.65	34.27	3.39	4.97	21.33	24.29	50.38	24.77
	Summerwood .....	2.69	5.26	24.15	4.07	3.37	21.50	19.35	58.45	21.24

<b>Red alder</b>						
Heartwood						
Springwood	3.02	4.01	20.49	3.69	5.18	22.37
Summerwood	3.03	4.16	21.15	3.60	5.55	23.36
White ash, sp. gr. 0.68						
Sapwood						
Springwood	8.84	10.99	23.71	3.11	5.49	21.45
Summerwood	6.13	8.18	19.32	2.76	5.44	20.51
White ash, sp. gr. 0.71						
Sapwood						
Springwood	4.04	4.95	17.71	2.76	6.34	20.34
Summerwood	2.90	3.57	14.57	2.49	6.01	19.35
White ash, sp. gr. 0.81						
Sapwood						
Springwood	7.35	8.38	22.95	2.74	5.80	20.17
Summerwood	6.85	7.34	19.64	2.41	5.74	20.52
						•

the heartwood and here the cellulose is correspondingly lower in the sapwood. Acetic acid obtained by hydrolysis is consistently higher in sapwood than in the heartwood of both softwoods and hardwoods.

### Analytical Differences in Spring- and Summerwood

The results of analyses of spring- and summerwood<sup>10</sup> are given in Table XXI. Lignin is present in larger amount in the springwood than in summerwood. This is explained by the fact that the middle lamella (which is composed of lignin) forms a larger portion of the wood substance in the cell walls of springwood than in the thick cell walls of summerwood. In general, the percentage of cellulose (both Cross and Bevan cellulose and pentosan-free cellulose) is appreciably higher in summerwood than in springwood, although there are a few exceptions to this rule.

### Summative Analytical Data

The following table (XXII) gives analytical data compiled by Dore<sup>11</sup> in his summative analyses of American woods.

TABLE XXII  
SUMMATIVE ANALYSES OF AMERICAN WOODS (DORE)

	Per Cent	Per Cent			Soluble	Pento-			Total
	Ex- tracted by Benzol	Ex- tracted by Alcohol	Cellu- lose	Lig- nin	sans (Xylan)	Man- nan	Galactan		
Redwood . . . . .	0.34	4.39	54.89	34.50	3.67	3.21	0.50	101.50	
Yellow pine . . . . .	2.22	1.49	57.72	29.47	3.49	6.37	0.78	101.54	
Sugar pine . . . . .	2.84	1.90	59.18	29.50	1.86	6.63	0.50	102.41	

It will be recalled that Dore's methods as applied to coniferous woods were unsuited to the analysis of hardwoods. The following data obtained by Dore on oak (*Q. agrifolia*) show the possibilities for summative analyses of hardwoods with the modified procedure referred to on page 126, Chapter 1. Benzene extract 0.52 per cent, alcohol extract 4.52 per cent; soluble in cold water 3.82 per cent; soluble in 5 per cent NaOH 19.53 per cent, cellulose 47.49 per cent; lignin 21.14 per cent; pentosans not otherwise accounted for 1.97 per cent; mannans (not extracted) none; galactans (not extracted) 1.56 per cent; total 100.55 per cent.

More interesting perhaps than the preceding data are those indicating the distribution of the furfural-yielding groups, methoxyl groups,

<sup>10</sup> Ritter and Fleck, *Ind Eng Chem*, 18, 608 (1926).

<sup>11</sup> *Loc. cit.*

and acid-yielding material (expressed as AcOH)—over the various constituents in redwood and oak.

As in the case of the results obtained in the Forest Products Laboratory, roughly 50 per cent of the total furfural-yielding components of wood remains in the Cross and Bevan cellulose. In the case of redwood, most of the remaining furfural-yielding material is removed by chlorination, while in the case of oak, the NaOH extraction which precedes the cellulose determination, evidently removes approximately 50 per cent of this material. Dore's method for the isolation of lignin gives a preparation practically free from pentosans. In the case of redwood the total methoxyl content of the wood is quantitatively recovered in the lignin fraction. In the case of oak, a part of the methoxyl is lost during the wood extraction (probably due to the action of alkali) but too much weight cannot be given to these quantitative data, since difficulty was experienced in obtaining concordant results in duplicate determinations.

TABLE XXIII

DISTRIBUTION OF GROUPS OVER THE CONSTITUENTS OF REDWOOD AND OAK (DORE)  
(Calculated on basis of the original dry wood)

	Furfural Yield	Per Cent Total Volatile Acid	Per Cent Methoxyl Groups
Redwood:	Untreated wood . . . . .	5.84	1.00
	Cellulose . . . . .	2.52	0.71
	Chlorination solutions . . .	2.15	—
	Lignin . . . . .	0.24	0.09
Oak:	Untreated wood . . . . .	12.90	Not determined
	Cellulose . . . . .	6.11	" " Not determined
	Chlorination solutions . . .	1.10	" " "
	Lignin . . . . .	None	3.53

#### Analytical Data Obtained on Foreign Woods

1. *German Woods.* The methods of Schwalbe and Becker gave rise to the results obtained in the following table (XXIV). In general, these results compare very favorably with those obtained at the Madison laboratories.

A totally different scheme of analysis led to the results of Konig and Becker.<sup>12</sup> Since the pure or "ortho" cellulose is determined by difference and as the determination of hemicelluloses is not a fixed procedure, but varies with the kind of wood examined, these results are not comparable with any of the foregoing. The data are actually the results of a summative analysis, quite different from the one devised by Dore. The only "overlapping" constituents are found in a part of the

<sup>12</sup> *Loc. cit.*

TABLE XXIV  
ANALYSIS OF EUROPEAN WOODS (SCHWALBE AND BECKER)

	Spruce ( <i>Picea excelsa</i> , Link)	Pine ( <i>Pinus syl- vestris</i> , L.)	Beech ( <i>Fagus sil- vatica</i> , L.)	Poplar ( <i>Populus tremula</i> , L.)	Birch ( <i>Betula alba</i> , L.)
Per cent ash..... . . . .	0.77	0.39	1.17	0.32	0.39
(a) Per cent ether soluble material ..... . . . .	0.78	1.92	0.31	1.08	0.71
(b) Per cent alcohol solu- ble material ..... . . . .	1.52	1.53	1.74	2.08	1.09
(a) + (b)..... . . . .	2.30	3.45	2.05	3.16	1.80
Per cent alcohol-benzol soluble .. . . .	2.34	3.32	1.20	2.87	1.68
Methyl number . . . .	2.36	2.20	2.96	2.56	2.77
Per cent pectin (von Fellen- berg's method)	1.22	1.11	1.75	1.82	1.61
Acetic acid (Schorger's acid hydrolysis) . . . .	1.44	1.40	2.34	4.17	4.65
Per cent nitrogen . . . .	0.11	0.13	0.17	0.10	0.12
Per cent protein . . . .	0.69	0.80	1.05	0.63	0.74
Per cent pentosans	11.30	11.02	24.86	23.75	27.07
Per cent methyl pentosan	3.00	2.23	1.02	0.72	0.84
Per cent Cross and Bevan cellulose . . . .	63.95	60.54	67.09	62.89	64.16
Per cent pentosan-free cel- lulose . . . .	57.84	54.25	53.46	47.11	45.30
Per cent lignin . . . .	28.29	26.35	22.46	18.24	19.56

pentosans, and if we add the percentages protein, ash, resin, total pentosans, hemicellular hexosans, lignin, and "purified" cellulose, the sum totals 100. Similarly if the percentages of protein, ash, resin, hemicellular hexosans and hemicellular pentosans, lignin and *crude* cellulose are added, the sum total is 100 per cent.

Within the past decade, fragmentary analytical data have appeared in the literature and only brief abstracts of some of the more recent results are given in following sections. No attempt has been made to give a complete compendium of analytical data.

*Argentine Woods.* Dominquez<sup>14</sup> has made a series of analyses covering 32 woods of trees native to Argentine. His determinations include: moisture, water-soluble matter, "tannins" and "non-tannins," and ash.

*Swedish Woods.* Wahlberg<sup>15</sup> reports investigations on Swedish pine and spruce woods. He determined the resin and cellulose contents. The latter was determined by the use of bisulfite followed by bromine.

*Japanese Woods.* Nakamura<sup>16</sup> reports the analysis of two coniferous woods from Karafuto: *Ezo-matsu* (*Picea ayacensis* Fisch) and (*Todo-*

<sup>14</sup> *Anales soc. quim. Argentina*, 5, 113 (1917)

<sup>15</sup> *Zellstoff u. Papier*, 2, 129-34, etc (1922)

<sup>16</sup> *Mem Coll Sci Kyoto, Imp. Univ.*, 6, 295 (1923).

TABLE XXXV  
RESULTS OF KONG AND BECKER'S SUMMATIVE ANALYSES OF EUROPEAN WOODS

*matsu* (*Abies sachaliensis* Mast.). The determinations included ash, protein, resin, lignin, pentosans, hexosans and cellulose. *Todo-matsu* contains more pentosans, hexosans, and less cellulose than does *Ezo-matsu*. Miura<sup>16</sup> determined the methoxyl content of 29 woods taken from the principal forest trees of Japan.

*British Colonial Woods.* Various woods of British Guiana were studied analytically.<sup>17</sup> The chemical analyses included per cent ash and cellulose and fiber lengths, the object being to evaluate the woods as raw materials used in papermaking. Analyses were also made of three woods from British Honduras.<sup>18</sup> Quam (*Schizolobium* sp.), white Moho (*Hibiscus* sp.?) and polak wood (*Ochroma* sp.) were thus examined.

A sample of wattlewood (*Peltorphorum africanum*) was analyzed by English<sup>19</sup> using Schorger's methods. On the oven-dry basis, the wood contained: 0.85 per cent ash, 9.55 per cent cold water-soluble matter, 12.29 per cent hot water-soluble matter, 0.17 per cent ether-soluble material, 4.19 per cent acetic acid, 21.2 per cent pentosans, 1.3 per cent methyl pentosans and 59.3 per cent Cross and Bevan cellulose (of which 9.42 per cent was pentosan).

*French West African Woods.* Heim and his collaborators<sup>20</sup> have obtained the following analytical data (Table XXVI) on oven-dried woods of W. Africa.

TABLE XXVI  
ANALYSIS OF WOODS FROM FRENCH W. AFRICA

Wood	Scientific Name	Per Cent Ash	Per Cent Resins, Fats, etc	Per Cent Cellulose	Per Cent Lignin
"Sibo" (Ivory Coast) . . . . .	<i>Sarcoccephalus esculentus</i> Afzel	0.2	0.96	67.48	31.36
"Fromager" (Gaboon) . . . . .	<i>Eriodendron anfractuosum</i> D. C.	5.9	0.62	68.3	25.18
"Bahia" (Gaboon) . . . . .	<i>Mitragyna macrophylla</i> Hiern	0.77	0.60	70.0	28.62
"Pri" (Ivory Coast) . . . . .	<i>Funtunia africana</i> Stopf	0.98	0.63	65.0	33.39
"Ako" (Ivory Coast) . . . . .	<i>Antiaris africana</i> Engler	1.57	0.54	65.0	32.89
"Samba" (Ivory Coast) . . . . .	<i>Triplochiton Johnsonii</i> C. H. Wright	1.77	0.56	59.0	39.0

# PART IV

## DECOMPOSITION OF WOOD

### Chapter I

#### Combustion of Wood

The combustion of wood holds two main lines of interest: (1) the condition under which the wood will ignite and burn, and (2) its heat of combustion. The former determines its value as a construction material exposed to fire hazards. The latter determines its fuel value. The first of these has not often had adequate discussion from all points of view.

#### Ignition Temperature

There have never been any satisfactory determinations of the ignition temperature of wood since the determinations have depended more on the surrounding conditions than on the wood itself. The method and rapidity of heating, the air supply, the place where the temperature is measured, and whether there is a pilot flame, are all factors which may greatly influence the ignition temperature. Good methods for determining the relative combustibility and perhaps the relative ease of ignition of different treated and untreated woods have been developed, but these do not necessarily show the actual minimum ignition temperatures of the woods tested. Consequently a theoretical discussion must suffice.

As we will see in the next chapter, wood begins to decompose at about  $275^{\circ}$  C. and that decomposition is exothermic in character. During the course of this decomposition combustible and incombustible gases and vapors are formed, and a combustible residue, charcoal, is left behind. Since there is no considerable decomposition of wood below this temperature, it would not be expected that the wood could ignite sooner because the oxygen of the air certainly could not combine directly with the solid wood substance at such low temperatures. The ignition temperature of all woods would be expected to be at about  $275^{\circ}$  C. under the optimum conditions. This theory probably holds except (1) as the physical properties of the wood, such as porosity, influence the surface of contact between the wood and air and (2) for the presence of

extractives with low ignition temperatures, such as volatile oils. If the ignition takes place at about 275° C. it means that the vapors or gases formed by the decomposition of wood by heat normally ignite at this temperature or that they ignite at a lower temperature than usual due to the catalytic action of the residue of charcoal, or else it means that the exothermic heat carries the temperature locally above 275° C. and starts the combustion. The ignition temperature cannot be much above 275° C. because if so it would be possible to distil wood to a residue of charcoal in the open air without combustion which seems impossible when the ready ignition of freshly formed charcoal is considered.

The actual final ignition temperature of wood is probably not affected by moisture content because the moisture will be removed before the wood has reached the ignition point, but the presence of moisture will naturally reduce the speed at which the wood is heated to the ignition temperature. The presence of solid combustible extractives with ignition points higher than that of wood would not appreciably affect the ignition of the whole. If there is a pilot flame for the ignition of combustible vapors the presence of considerable amounts of turpentine or other volatile oil in wood might cause ignition below 275° C. but without the presence of volatile oil destructive distillation probably precedes combustion.

### Mechanism of Combustion of Wood

With these conclusions in view it is possible to discuss the combustion of wood in more detail. Leaving out of consideration the presence of extractives, let us consider how wood ignites and burns. When combustion is once started it keeps itself going so long as there is enough air supply and so long as the heat of combustion is not dissipated but used to heat new portions of the wood up to the ignition temperature. It needs no discussion to show that a sufficient air supply is required to keep the combustion going, but it may need some explaining to show how a piece of wood once ignited and burning may become extinguished without any external changes in conditions.

The combustion of wood may be considered to take place in two stages: 1st, the combustion of gases and vapors given off by the exothermic decomposition of wood and 2nd, the combustion of the solid residue of charcoal left behind after the exothermic reaction is finished. These stages may not be sharply defined since volatile combustible material is driven off from the original charcoal if it is further heated after the completion of the exothermic reaction but there is certainly a change in the character of the combustion at about this time. This is further indicated by the fact that about half the vapors and gases given off during the exothermic reaction are incombustible ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ), while

nearly all the gases given off afterward are combustible. It can readily be conceived therefore that the outside of a large stick of wood may be heated to the ignition temperature and burn through the first stage of combustion without heating the interior of the stick above 275° C. On account of the low conductivity of charcoal, the heat from the combustion of the charcoal on the outside of the stick may not be conducted inward rapidly enough to heat more wood to the distilling point and the "fire may go out." This accounts for the difficulty in burning large chunks of wood, such as stumps or logs, unless the conditions are such as to keep the heat from being radiated away. A large pile of stumps may be burned without much difficulty but the burning of a single stump is a hard job. "One piece of wood keeps another afire."

This property of burning rapidly on the outside, charring a thin layer, and then being extinguished entirely or burning very slowly is a valuable one for wood used for construction work exposed to fire hazards. In fact steel under the same conditions and carrying the same load may be rapidly heated through and not infrequently may lose its strength and drop its load sooner than the wooden member.

### Heat of Combustion

The heat of combustion of wood has been the subject of many determinations, but most of them were made before accurate methods of calorimetry were available or before it was realized that a careful control of the moisture in the test pieces was necessary. Some of the first work that was at all reliable was by Gottlieb<sup>1</sup> and from that time to the recent work of Parr and Davidson<sup>2</sup> nothing was done on the subject. This last work was done on samples of known moisture content and by the most modern and accurate methods and the determinations on duplicate samples agree very closely so that the results can be considered authoritative. The only correction which might be made on these results is for the amount of heat required to remove the adsorbed water from the wood.<sup>3</sup> It has been shown that this amounts to about 35 B.t.u. per pound of saturated wood but it would be less than this in the figures given for dry wood since the samples used were only partly saturated. The averages of Parr's results for each of six species of wood are given in Table XXVII.

Only one species of resinous wood, pine, is included but it will be noticed that this gives a higher calorific value than any of the non-resinous

<sup>1</sup> *J. prakt. Chem.*, **28**, 414 (1883).

<sup>2</sup> *J. Ind. Eng. Chem.*, **14**, 935 (1922). This article contains a brief bibliography and discussion of former work.

<sup>3</sup> See p. 286.

TABLE XXVII  
FUEL VALUE OF WOOD

Species	Moisture Content	B.t.u. per Lb. (Moist Wood)	B.t.u. per Lb. (Dry Basis)
Pine . . . . .	8.88	8049.8	8836.2
Oak . . . . .	8.35	7841.5	8555.7
Hickory . . . . .	10.30	7578.0	8448.1
Cherry . . . . .	8.85	7859.9	8623.0
Birch . . . . .	10.18	7597.4	8458.4
Poplar . . . . .	10.69	7716.1	8639.6

woods. This can be readily accounted for by the presence of resin in the pine. On account of the high fuel value of resin (17,400 B.t.u. per pound computed from 20 per cent terpenes and 80 abietic acid by the Du Long formula) a small proportion of resin in wood may make considerable increase in its fuel value. If, for instance, a wood contained 5 per cent resin, its fuel value would be  $.05 \times 17,400 + .95 \times 8600 = 9040$  B.t.u. per pound. Aside from this difference due to resin content we have no other apparent relationship between chemical composition and calorific value. The slight difference between the hardwoods shown in Table XXVII (a maximum of 2.3 per cent) can be accounted for by variation in amount and composition of the extractives. If we assume, for instance, that the cell wall proper of species A is 90 per cent and of species B is 95 per cent and of a calorific value 8600 B.t.u. per pound in both cases, while the 10 per cent extractives of A have a value of 6000 B.t.u. per pound and of B 7000 B.t.u. per pound, then A will have a total value of  $(90 \times 8600) + (10 \times 6000) = 8340$  and B,  $(95 \times 8600) + (5 \times 7000) = 8520$  or a difference of over 2 per cent.

It is not known what effect the differences in composition between softwoods and hardwoods aside from the resin content of the former may have on the calorific value. In fact there is a good field for research in the accurate determination of calorific value of samples whose chemical composition has been determined and possibly modified by extraction or otherwise.

#### Effect of Moisture

In these discussions the moisture content of the wood has not been included since dry wood has been assumed in all examples. Moisture is, however, of great importance and since it is commonly present in wood it will be given a discussion by itself. It will be noticed that the determinations shown in Table XXVII were made on wood containing moisture and then corrected by simply dividing the value obtained by [100—the moisture content]. This is correct<sup>4</sup> in this case where the moisture

<sup>4</sup> Except for the comparatively small amount of heat required to remove the adsorbed water from the wood.

evaporated by the combustion is condensed and its latent heat recovered but in a practical use of wood as fuel where it is used to heat a material above the boiling point of water (or where the waste flue gases contain the moisture in vapor form) this method of correction is not sufficient. In such a case the moisture not only reduces the value of the fuel by so much inert material but also causes a loss of the heat required for heating it to 100° C., for its evaporation, and for heating its vapor to the temperature of the escaping flue gases. For example, one pound of wood with 5 per cent moisture will have an actual fuel value equal to

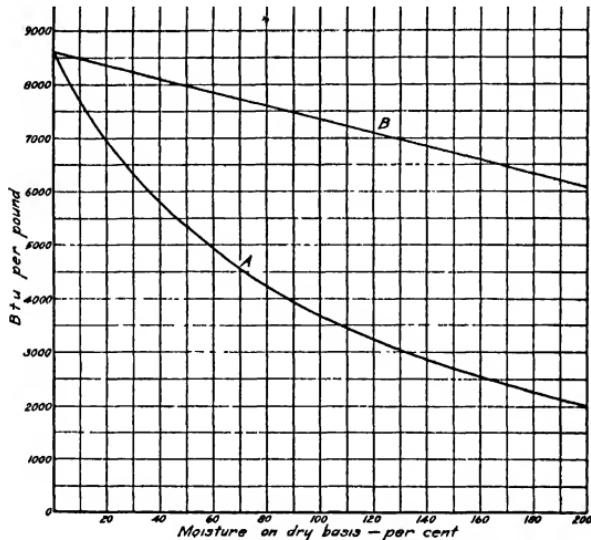


FIG. 10.—Relation between Moisture Content and Fuel Value of Wood.

that of 0.9524 pound of wood minus the specific heat of 0.0476 pound of water between 70° and 212° F. minus the heat of evaporation of 0.0476 pound of water and minus the specific heat of 0.0476 pound of steam between 212° F. and, say, 500° F.<sup>6</sup> Fig. 10 shows the effect of different percentages of moisture on the fuel value of the wood calculated like the above example. It should be noted that the moisture figures in this figure are on the basis of dry weight of wood—that is 50 per cent moisture means 50 parts water to 100 parts dry wood. In

<sup>6</sup>The amount of heat required to heat the air necessary for the combustion to the temperature of the flue gases should also be included here in order to give complete figures on fuel value. This factor is, however, a constant and does not affect the relative values of wood with different moisture contents.

curve A, which shows the variation of fuel value per pound of wet wood burned, the fuel value diminishes rapidly at first and then more slowly so that at a moisture figure of 100 per cent (100 parts wood to 100 parts water) the value is still 3,670 B.t.u. per pound. This method of computing fuel value on the basis of B.t.u. per pound of *wet* wood is likely to be misleading, since it does not furnish direct information in regard to the variation of the fuel value of a given quantity of wood with variations in moisture content, as for instance, the increase in fuel value of a cord of wood with 35 per cent moisture when it is dried to 15 per cent moisture. For the purpose of showing this kind of change Curve B was drawn which shows the change with moisture content of the B.t.u. per pound of *dry* wood. This curve shows that a pound of dry wood with 0.35 pound moisture has a fuel value of 8,163 B.t.u. while with a decrease to 0.15 pound moisture the fuel value has been increased to 8,413 B.t.u. or by only 3.0 per cent.

This method of computing change in fuel value with change in moisture is probably correct for low moisture contents but other factors apparently become important with high moisture contents. From the curve B in Fig. 10 it would appear that wood with 200 per cent moisture still had a considerable fuel value—6,100 B.t.u. per pound in comparison with 8,600 for dry wood, but from the practical standpoint wood with twice its weight of water is about the limit that can possibly be burned, even in specially constructed furnaces for using wet fuel. This is not because the fuel value is not present but because it is difficult to dry such wet wood in the fire box under the conditions required for propagating combustion in the mass of fuel.

#### Commercial Wood Fuels

As in many other cases the relative fuel value of different woods per pound is not the same as the relative values per cord on account of the variation in the specific gravity and correspondingly in the weights per cord. For instance, a cord of pine may not be as valuable for fuel as a cord of hickory notwithstanding the figures in Table XXVII, since the cord of hickory may weigh enough more than the cord of pine to make up and over-balance the high value of the pine wood per pound.

It is not often that wood actually competes on an even basis with other fuels in the United States. Where wood is used as an industrial fuel for power generation, as in sawmills or wood-working plants, there is a sufficient quantity of fuel wood which would otherwise be a waste, as for instance, the sawdust, shavings and small edgings and trimmings. At sawmills located in small towns there is little demand for industrial fuel other than in the mill itself, and there is frequently a surplus even after the demands for domestic fuel have been met. Wood is so low grade

a fuel compared with coal or oil that its transportation over any considerable distance is not profitable. At sawmills located in cities the surplus mill waste can be sold for industrial or domestic fuel and here there may be some competition between wood and other fuels.

The big bulk of the wood used for domestic fuel consists of fire-wood cut from the farmer's wood lot and used mostly by the man who cuts it. The use of wood as a domestic fuel in towns and cities is mostly a luxury and the wood does not compete with other fuels on a basis of calorific value.

For industrial fuel wood is now commonly used in form of sawdust or "hogged" chips small enough so that they may be handled on conveyors. For this kind of fuel, which is usually wet, a special type of fire-box, the "Dutch oven," is used. This is a large brick fire-box fed from the top with the fuel forming large cones on the grates. It must be of sufficient size and proper construction so that the fine, damp fuel is dried, heated through, and burned before it is carried to the flues by the draft. This is accomplished by having a large area of radiating surface in the fire-box itself and by preventing direct radiation from the burning fuel to the surface to be heated.

### Wood Ashes

At one time the ashes obtained by the combustion of wood were of considerable importance as a source of potash; in fact it is hardly a century ago that in newly settled localities in this country the chief value of wood lay in its potash content. The pioneers in clearing their land piled the logs until they were dry enough to burn and after burning carefully collected the ashes. This was frequently the first valuable product from the land and the only one with a cash value. For many years after this period wood ashes were sufficiently valuable to pay for their collection and use as fertilizer or as a source of crude potash. Perhaps even today some home-made soft soaps require the saving and leaching of ashes from the farmer's stove.

Since the commercial production of potassium salts from the Stassfurt deposits the value of wood ashes has diminished and they are no longer an article of commerce. In most places where large amounts of wood are burned as in sawmill power plants or in waste burners, the draft through the fire-box is so rapid that the ashes go out with the smoke. Where wood is used in small amounts as for domestic fuel the cost of collection of the ashes is prohibitive.

## Chapter 2

### The Decomposition of Wood by Heat

The decomposition of wood by heat is of interest largely for the reason that it forms the basis of the wood distillation industry. In this chapter only the chemical side of the destructive distillation itself will be covered, and discussion of the refining process, and of the engineering and economics of the industry will be omitted, since these subjects do not have any bearing on the chemistry of wood. Readers interested in these subjects are referred to the special literature of wood distillation.<sup>1</sup>

The decomposition of wood by heat under ordinary conditions and in reasonable time is not serious until about 275° C. is reached. The water is driven off long before this temperature is reached and likewise various extraneous materials may be volatilized or decomposed but the change in chemical composition of the wood fiber itself is not marked. Slight chemical changes resulting in marked physical changes as in strength or color may take place at lower temperatures and in the artificial drying of wood the temperatures are usually kept below 90° C. in order to avoid decrease in strength. It is possible also that long-continued action of medium high temperatures may have very nearly the same results as higher temperatures for a short time. The slow darkening and final charring of wood in contact with steam pipes is a good example, but no quantitative study of this effect has been made.

Any accurate determination of the effect of temperature on wood is difficult on account of its very low conductivity. Even with a small piece of wood and with slow heating it is difficult to have all parts of the wood heated to the same temperature at the same time and an observed effect may be due to a small part of wood which is at the maximum temperature while most of the wood is still many degrees cooler. The latest and best work on this subject is that of Klason, von Heidenstam and Norlin<sup>2</sup> in which small charges of wood were heated with careful temperature control and with measurement of the temperature at the center and surface of

<sup>1</sup> Hawley, "Wood Distillation," 1923, Chemical Catalog Co. Bunbury, "The Destructive Distillation of Wood," 1923, Benn Bros., London Bergstrom and Wesslén, "Om Trakohning," 1918, Nordstadt & Soner Klar, "Technologie der Holzverkohlung," 1910, Julius Springer.

<sup>2</sup> *Arkiv Kemi, Mineral. Geol.*, 3, 1-34 (1908); *Z. angew. Chem.*, 27, 1205 (1909), and 27, 1252 (1910).

the charge. A typical record of such a distillation is shown in Fig. 11. It will be noted that although the outside temperature rose rapidly to about  $290^{\circ}$  at the end of the second hour, yet there was very little decomposition of the wood as shown by the products. The liquid distillate was mostly water as shown by the inside temperature and by the fact that the rate of flow diminished after  $1\frac{1}{2}$  hours. The presence of a little combustible gas is difficult to explain but this also *diminishes* up to the second hour, showing that it is not a part of the main reaction which begins later. After about two hours the water in the wood is apparently all driven off, and although the outside temperature has been and remains

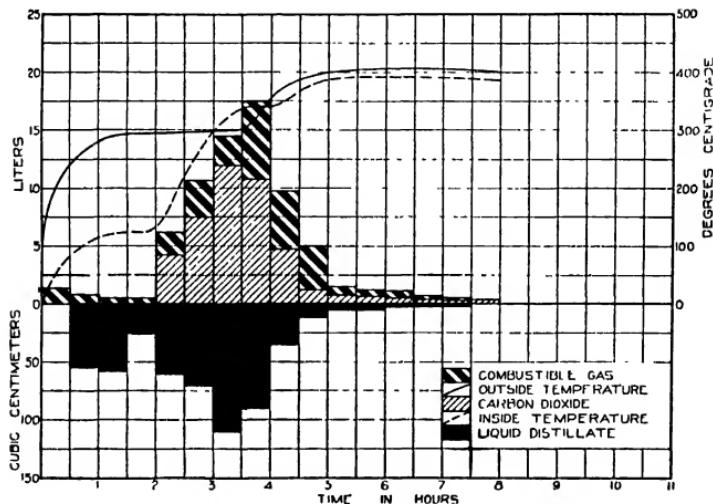


FIG. 11.—Relation between Temperature, Time, and Products, in the Decomposition of Wood by Heat.

nearly constant between  $290^{\circ}$  and  $300^{\circ}$  C., the inside temperature now rises rapidly. The main reaction now begins with formation of large quantities of combustible gas and carbon dioxide and the liquid distillate contains acetic acid, tar, and methanol (although these constituents are not shown in the figure). From these curves the exact point where active decomposition begins cannot be determined since the two temperature curves are so far apart and since the maximum temperature has been nearly constant for half an hour without much effect. It can only be said to be near, but below, the maximum temperature of  $290^{\circ}$  C. but other observations by Klason have placed it at about  $280^{\circ}$  C.

The rapidly rising inside temperature soon becomes higher than the

outside temperature showing the exothermic character of the reaction. The exothermic reaction is quickly finished, as shown by the outside temperature becoming the higher again, and by the marked decrease in the gases and the liquid distillate.

The exothermic reaction has been further studied by K'fason<sup>3</sup> giving other details of the manner in which wood decomposes with heat. In a small apparatus in which all the conditions could be accurately controlled, he distilled wood (1) in vacuum and rapidly (2) at atmospheric pressure and very slowly (14 days' distillation). In the first case, the secondary reactions (decomposition by heat of products first formed, or interaction between products) were kept at a minimum since the volatile products were removed from the distilling vessel and cooled in the minimum possible time. In the second case, the conditions were just the opposite and the secondary reactions were allowed to run to the limit. The most marked differences in the results of these distillations were in the amounts of charcoal, tar, and gas formed and in the fact that no exothermic reaction developed in the vacuum distillation. In the vacuum distillation the yield of tar was very much higher than usual and the charcoal and gas correspondingly lower. In the long, continued distillation at atmospheric pressure the charcoal and gas were higher than usual while the tar was very much lower. The vacuum tar was also unusual in its light color and translucence and in that it decomposed exothermically at 280° C. into ordinary tar, gas, and coke.

These results show that the primary reaction consists in the formation of primary tar and primary charcoal but that under ordinary conditions of distillation the former decomposes as rapidly as formed into secondary tar and gas, which are among the volatile products, and a tar coke, which is deposited in the charcoal. Since ordinary wood charcoal shows no marked difference between the surface and the center of the lumps, these secondary reactions must take place almost simultaneously with the primary reaction. The primary decomposition of wood is not exothermic, but a secondary reaction which takes place almost simultaneously is the cause of the exothermic character of the ordinary destructive distillation of wood.

This conception of ordinary charcoal as a primary charcoal on which, or in which, secondary charcoal or tar coke has been deposited is of interest in connection with the activation of charcoal. Ordinary charcoal is a poor adsorbent of gases and it must be activated by selective oxidation in order to make it highly adsorbent and it seems reasonable that this oxidation removes the tar coke leaving the primary charcoal. This hypothesis could be readily tested by determining the adsorbent power of charcoal prepared by distillation in vacuum. It has been claimed that

<sup>3</sup> *J. prakt. Chem.* (2), 90, 413 (1914).

the charcoal obtained by distilling wood in a current of superheated steam is much more adsorbent than ordinary charcoal and if this is true it tends to confirm the hypothesis since the superheated steam would have somewhat the effect of a vacuum in rapidly removing the primary products before they had time to decompose. This hypothesis is not so much at variance with that of Chaney<sup>4</sup> as an addition to it. He assumes charcoal to be "a stabilized complex of hydrocarbons adsorbed in a base of active (absorptive) carbon." If we assume that the primary charcoal is the adsorbent charcoal and that the activation consists in the removal of the secondary tar coke as well as adsorbed hydrocarbons, then Chaney's hypothesis is correlated with Klason's experimental results.

The formation of charcoal from a more or less physical standpoint has also been studied by Hawley<sup>5</sup> who found that the physical characteristics of the charcoal could be modified by mechanical means during the decomposition of the wood. Ordinary charcoal preserves to a certain extent the structure of the wood from which it is formed, so that it is frequently possible to determine the species of wood by microscopic examination of the charcoal. The charcoal, however, is shrunken in volume and the original wood structure may be distorted. By careful application of mechanical, not pneumatic, pressures of about 100-120 pounds per square inch during the decomposition of the wood, the charcoal could be made much denser and frequently the original structure of the wood was entirely obliterated, the charcoal having a conchoidal fracture and being translucent in thin sections. There is evidently a stage during the decomposition of wood by heat when the mass is slightly plastic. It was also found that denser charcoal could be made from a partly hydrolyzed wood.

The ordinary decomposition of wood by heat may be roughly divided into three stages: (1) before, (2) during, and (3) after the exothermic reaction. The first stage is not important since it consists mostly in drying the wood, and water is the main product, but it has been shown<sup>6</sup> that a small amount of acetic acid and a trace of methanol are formed during this period. This is probably a result of hydrolysis rather than of straight heat decomposition. During the second stage the main part of all the products is given off, with the probable exception of hydrogen. It is doubtful whether hydrogen is a product at 300-350° C. After the exothermic reaction is finished further heating of the charcoal gives only gas<sup>7</sup> with traces of tar and methanol<sup>8</sup>.

<sup>4</sup> *Trans Am Electrochem Soc.*, **36**, preprint (1919).

<sup>5</sup> *J. Ind. Eng. Chem.*, **13**, 301 (1921).

<sup>6</sup> Hawley and Palmer, Dept. Agr. Bull. No. 129.

<sup>7</sup> "Om Trakolning," pp. 174 and 180.

<sup>8</sup> Hawley, *Ind. Eng. Chem.*, **15**, 697 (1923).

### Products of Wood Distillation

The products of wood distillation separate naturally according to their solubility and volatility, into four groups, charcoal, tar, pyroligneous acid, and gas.

(1) The charcoal contains the non-volatile products except those which may be carried away mechanically in the vapors and also contains certain volatile products which are held behind by adsorption in the solid charcoal.<sup>9</sup>

(2) The settled tar consists mainly of the non-volatile material carried over mechanically in the form of tar fog and of those volatile constituents not soluble in the pyroligneous acid. There is also a kind of tar called "dissolved tar" which dissolves in the pyroligneous acid but remains behind when the latter is distilled.<sup>10</sup>

(3) The pyroligneous acid contains the water-soluble volatile constituents and those rendered soluble by the presence of the other solvents such as methanol and acetic acid. Since the pyroligneous acid and the tar form two liquid layers there is a solubility equilibrium between them and any of the main constituents of one may possibly be found in small amounts in the other. For instance, water, methanol, and acetic acid are found in the tar.

(4) The gas consists mainly of the uncondensable gas constituents but it is also saturated with vapors of the more volatile liquids of the pyroligneous acid and carries a small amount of a fog of the less volatile constituents.

These four crude products of wood distillation vary in amount depending on the species of wood and on the conditions of distillation but the average yields from hardwoods at atmospheric pressure and 350-400° C. maximum temperature are about 38 per cent charcoal, 9 per cent total tar, 33 per cent pyroligneous acid (after distillation to remove dissolved tar) and 20 per cent gas. Since it is not intended to discuss the refining processes and since many of the simple constituents may be found in more than one of the crude products the composition of the latter will not be described in detail.

Following is a list of the chemical individuals which have been identified among the products of wood distillation. This does not contain the constituents from resinous wood distillation which are obviously products of the distillation of the resin such as terpenes and rosin acids.

## PRODUCTS OF WOOD DISTILLATION

Carbon dioxide	Valeric aldehyde	Di-methyl ether of
Carbon monoxide	Furfural	methyl pyrogallol
Methane	Methyl furfural	Di-methyl ether of
Hydrogen	Acetone	propyl pyrogallol
Water	Methyl ethyl ketone	Creosol <sup>12</sup>
Formic acid	Di-ethyl ketone	Eugenol <sup>13</sup>
Acetic acid	Methyl propyl ketone	
Propionic acid	Methyl butyl ketone	Ammonia
Butyric acid	Ethyl propyl ketone	Methyl amine
Valeric acid	Cyclopentanone	Pyridine
Caproic acid	Methyl cyclopentanone	Methyl pyridine
Crotonic acid	Adipic ketone	
Angelic acid	Di-acetyl	Pyro xanthone
Pyromuic acid	Phenol	Methylal
Lignoceric acid	o-m- and p-cresol	Di-methyl acetal
Valerolactone	Phlorol	Di-methyl furane
Methyl alcohol	1-3 xylenol-5	Tri-methyl furane
Allyl alcohol	Pyrocatechol	Sylvane
Isoamyl alcohol	Guaiacol	$\alpha\alpha'$ -dimethyl tetrahydro-furane
Isobutyl alcohol	Ethyl guaiacol	$\alpha$ -methyl- $\alpha$ '-ethyl
$\text{CH}_2\text{---CH(OH)} --- \text{CH}\cdot\text{CH}_3$	Di-methyl ether of homopyrocatechol	$\alpha\beta'$ -dihydrofurane
Formaldehyde	Coerolignol	m-xylene
Acetaldehyde	Pyrogallol <sup>14</sup>	Toluene
	Di-methyl ether of pyrogallol	Melene $\text{C}_{10}\text{H}_{16}$ <sup>15</sup>

Lævoglucosan is probably a product of the distillation of wood in vacuum but it is not likely to be among the products obtained by distillation at atmospheric pressure (see p. 205).

These products belong mostly to a few groups of related compounds.

- (1) Acids mostly of the acetic acid series but with some unsaturated acids and one with a furane ring.
- (2) Alcohols, one unsaturated.
- (3) Ketones mostly of the acetone series but some cyclic and one di-ketone.
- (4) Aldehydes, formaldehyde series and with furane rings.
- (5) Phenols and phenol methyl ethers, mostly methyl ethers of di- and tri-phenols.
- (6) Ammonia derivatives.
- (7) Hydrocarbons of the benzene and furane series.

<sup>11</sup> Williams, Laselle and Reed have recently shown [*Ind Eng Chem.*, 17, 851 (1925)] that pyrogallol is probably absent and that 1-monomethyl ether of pyrogallol is probably present.

<sup>12</sup> Eugenol has been identified only in the tar from lignin distilled at reduced pressure, but it may be present in the products obtained at ordinary pressure. See also Chapter 3, part II.

<sup>13</sup> Melene and other hydrocarbons of the hydro-aromatic series have been reported by Pictet and Gaulis [*Helv. Chim. Act.*, 6, 627 (1923)] in the tar from lignin distilled at reduced pressure. Melene may be the main constituent of the paraffin-like substance reported frequently in wood distillation products.

TABLE XXXVIII  
YIELDS OF ALCOHOL AND ACID FROM VARIOUS SPECIES AND FORMS OF WOOD

Species	Locality	Methanol 100 Per Cent				Total Acid as Acetic					
		Heart-wood	Slab-wood	Heart and Slab	Other Forms	Per Cent	Per Cent	Heart-wood	Slab-wood and Slab	Other Forms	Per Cent
Beech	Indiana	1.95	1.79	1.87	Park Sapwood	1.25	5.56	6.18	5.87	Bark Sapwood	2.93
"	Pennsylvania	2.23	2.09	2.16	—	—	5.77	6.21	5.99	—	—
Birch	Wisconsin	1.45	1.55	1.54	—	—	6.71	6.88	6.80	—	—
"	Pennsylvania	1.62	1.59	1.60	—	—	6.19	6.10	5.42	Bark	—
Maple	Wisconsin	1.94	1.91	1.93	Bark	1.88	5.42	5.11	5.24	—	5.15
"	Pennsylvania	1.94	1.78	1.86	—	—	5.66	5.44	5.55	—	—
Red Gum	Missouri	1.76	1.73	1.75	—	—	5.70	5.23	5.46	—	—
Chestnut	New Jersey	0.90	0.87	0.89	Limbs	0.96	5.50	5.26	5.36	Limbs	6.42
Hickory	Indiana	2.08	—	—	—	—	5.05	—	—	—	—
White Oak	Indiana	1.34	1.33	1.33	—	—	4.97	4.77	—	—	—
"	Arkansas	1.33	1.46	1.39	—	—	4.23	4.35	4.29	—	—
Tupelo	Missouri	1.56	1.86	1.71	Limbs	1.64	4.49	5.19	4.84	Limbs	5.64
White Elm	Pennsylvania	2.12	1.68	1.90	—	—	6.39	6.61	6.50	—	—
Slippery Elm	Wisconsin	2.03	1.79	1.91	—	—	5.77	5.53	5.65	—	—
Silver Maple	Wisconsin	1.69	1.77	1.83	—	—	6.30	5.31	5.81	—	—
Green, Blue and Yellow Ash	Tennessee	1.91	1.43	1.67	—	—	4.64	4.14	4.39	—	—
Black Ash	Wisconsin	1.79	2.04	1.91	—	—	5.65	5.16	5.40	—	—
Green Ash	Missouri	—	—	—	Limbs	2.02	—	—	—	Limbs	4.51
Chestnut Oak	Tennessee	1.22	1.30	1.27	—	—	4.88	4.91	4.90	—	—
Tanbark Oak	California	1.72	—	—	—	—	6.89	6.01	—	—	—
Black Oak	California	—	1.53	—	—	—	—	—	—	Limbs	6.76
Swamp Oak	Louisiana	1.50	1.31	1.40	—	—	4.90	5.43	5.16	—	—
Eucalyptus	California	1.33	1.68	1.50	—	—	4.58	5.31	4.94	—	—

TABLE XXIX  
YIELDS OF PYROLIGNEOUS ACID, CHARCOAL AND TAR FROM VARIOUS SPECIES OF WOOD

Species	Pyrolygenic Acid				Charcoal				Tar			
	Tar-free and Without		Moisture in Wood		Heart		Slab		Heart		Slab	
	Heart	Slab	Mean	Heart	Slab	Mean	Heart	Slab	Mean	Heart	Slab	Mean
Beech	32.3	35.4	33.8	43.1	39.4	41.2	9.7	10.6	10.1	Indiana	Pennsylvania	Indiana
"	35.9	35.2	35.5	40.6	42.3	41.4	9.1	10.9	10.0	Pennsylvania	Wisconsin	Pennsylvania
Birch	34.2	34.4	34.3	39.0	38.1	38.5	9.6	8.5	9.0	Wisconsin	Pennsylvania	Wisconsin
"	37.1	33.6	35.3	36.4	38.6	37.9	12.6	10.3	11.4	Pennsylvania	Wisconsin	Pennsylvania
Maple	33.2	31.5	32.4	39.8	44.9	42.3	12.4	9.2	10.8	Wisconsin	Pennsylvania	Wisconsin
"	33.4	34.6	34.0	40.2	37.6	38.9	12.5	12.3	12.4	Pennsylvania	Indiana	Pennsylvania
Red Gum	38.2	32.0	35.1	36.8	47.4	42.2	11.7	7.5	9.6	Missouri	Arkansas	Missouri
Chestnut	36.1	29.4	32.8	47.6	52.9	50.4	4.7	3.7	4.2	New Jersey	Tennessee	New Jersey
Hickory	37.5	—	37.7	—	—	—	—	—	—	Indiana	Indiana	Indiana
White Oak	32.7	31.1	31.9	49.5	50.5	50.0	6.3	4.6	5.4	Arkansas	Arkansas	Arkansas
"	35.5	34.4	34.9	42.0	46.2	44.1	9.3	8.7	9.0	Missouri	Missouri	Missouri
Tupelo	35.4	34.9	35.2	45.9	46.1	46.0	11.4	12.1	11.7	Pennsylvania	Wisconsin	Pennsylvania
White Elm	35.6	37.5	36.5	40.0	39.7	39.8	12.1	11.1	11.6	Wisconsin	Wisconsin	Wisconsin
Slippery Elm	33.9	31.5	32.7	40.7	44.0	42.4	9.6	7.0	8.3	Wisconsin	Wisconsin	Wisconsin
Silver Maple	36.8	32.4	34.6	41.2	44.6	42.9	12.1	8.0	10.1	Tennessee	Tennessee	Tennessee
Green, Blue and Yellow/ Ash	33.8	28.8	31.3	41.0	45.8	43.4	11.3	7.9	9.6	Arkansas	Arkansas	Arkansas
Black Ash	35.1	34.1	34.6	38.2	40.5	39.3	11.4	9.1	10.2	Missouri	Missouri	Missouri
Green Ash	—	—	30.7	—	—	40.4	—	—	—	Tennessee	Tennessee	Tennessee
Chestnut Oak	35.6	29.8	32.7	39.6	46.9	43.2	10.2	8.8	9.5	California	California	California
Tanbark Oak	37.2	—	—	37.6	—	—	9.0	—	—	Louisiana	Louisiana	Louisiana
Black Oak	—	34.0	35.1	—	41.9	40.6	—	—	—	California	California	California
Swamp Oak	31.7	29.8	30.7	46.5	47.4	46.9	7.3	8.9	8.1	California	California	California
Eucalyptus	32.7	33.8	34.9	48.2	44.2	46.2	3.7	8.8	8.3	California	California	California

Many esters have also been identified but it is not necessary to enumerate them since all possible combinations of the acids and alcohols may be present in equilibrium amounts. There are also many unidentified products especially in the alkali-insoluble portions of the tar oils and in the non-volatile part of the tar. It has been shown<sup>14</sup> that acetone is not a primary product of the distillation, but is a decomposition product of the acetic acid first formed. The same is probably true of the formation of the higher ketones from their corresponding acids.

### Quantity of Certain Products

Quantitative yields are available only on the crude products and on a few of the chemical individuals as methanol, acetic and formic acids, methane and carbon dioxide. Tables XXVIII and XXIX show the yields of methanol, total volatile acid calculated as acetic, pyroligneous acid, charcoal, and tar from various forms and species of American hardwoods. The figures were all obtained from distillations under similar conditions in a gas-fired retort holding about 100 pounds of wood.<sup>15</sup> Similar figures are not available for softwoods but in general the yields of both methanol and acetic are one-half those from hardwoods. Carbon dioxide, carbon monoxide, and methane vary with the maximum temperatures of distillation but at 350°-400° C. the yields from hardwoods are about 8 per cent, 4 per cent, and 1.5 per cent respectively. The yield of water, aside from that occurring as such in the wood, runs from 22.3 per cent to 27.8 per cent according to Klason<sup>14</sup> and these figures correspond fairly well with those obtained by subtracting the alcohol and acetic acid from the pyroligneous acid in Table XXIX which gives a remainder that is mostly water. Formic acid in vacuum distillation may be formed in quantities as high as 35 per cent of the acetic acid<sup>14</sup> but in ordinary distillation at atmospheric pressure it varies from 10 to 20 per cent of the acetic acid.<sup>16</sup>

The other constituents shown in the list occur only in very small quantities, the total of the phenol-methyl-ether group making up only about 1 per cent of the weight of the wood distilled and the total ammonia group probably less than 0.2 per cent.

### Relation of Composition of Wood to the Products of Distillation

This subject is best developed by recounting what little has been done on the distillation of cellulose and lignin by themselves and filling in the rest of the picture by hypothesis. The subject is rendered difficult by the lack of knowledge of the composition of the celluloses distilled and by

<sup>14</sup> Klason, *loc. cit.*

<sup>15</sup> Hawley and Palmer, Dept. Agr. Bull. 129. Palmer, Dept. Agr. Bull. 508.

<sup>16</sup> Palmer, *J. Ind. Eng. Chem.*, 10, 262 (1918).

the possibility that the lignin had been modified by the process of isolation. Also the cellulose and lignin do not make up the whole of the wood substance and other constituents must be the source of certain products.

In connection with his first work in wood-distillation, Klason<sup>17</sup> distilled several kinds of cellulose and analyzed the products in comparison with wood-distillation products obtained under the same conditions. The main differences were found in yields of the products shown in Table XXX. In general the yield of charcoal from the wood was slightly higher than from the cellulose, although there is one exception in the case of birch. This will be discussed in more detail later. The same is true with the tar, birch being the only exception to the rule of higher yields from the wood. The unusually high yield of tar from pine wood is undoubtedly due to resin.

Methanol is found only in traces in the cellulose products and these traces may be due to small residues of lignin in the impure wood celluloses used. The source of the methanol is, therefore, the lignin as might be expected from the presence of methoxyl groups. (There is however, no direct relation between the amount of methoxyl in a wood and the amount of methanol which may be obtained by distillation.)

The acetic acid yields show that although some acetic acid comes from the cellulose, the wood gives very much more. It is also interesting to note that the hardwood celluloses give more acetic acid than the cotton or softwood celluloses, in keeping with the higher yields from the hardwoods. Klason suggested that this pointed to the pentosans in wood as the source of much of the acetic acid on distillation.

The methane is also higher in the woods than in the celluloses as might be expected if the methoxyl groups are the source of the methane. The yields of methane from cellulose agree closely with those obtained by Hawley and Aiyar,<sup>18</sup> but these authors obtained considerably more methane from wood, as much as 16 per cent in the case of incense cedar.

More recently Fischer and Tropsch<sup>19</sup> have reported the distillation of cellulose, wood and lignin, under the same conditions and the examination of the products. The distillations were made under reduced pressure so that the results cannot be compared with those of Klason. Unfortunately also, the cellulose used was described only as a bleached commercial pulp and there is no analysis of it, or even a statement as to what species of wood it came from. The results of these distillations are shown in Table XXXI. The charcoal is seen to be low from the cellulose, high from the lignin, and intermediate from the wood and this

<sup>17</sup> *Loc. cit.*

<sup>18</sup> *J. Ind. Eng. Chem.*, **14**, 1055 (1922).

<sup>19</sup> *Ber.*, **56B**, 2418 (1923).

TABLE XXX  
YIELDS FROM THE DESTRUCTIVE DISTILLATION OF WOODS AND CELLULOSES

	Cotton Cellulose	Pine Cellulose	Wood	Spruce Cellulose	Wood	Birch Cellulose	Wood	Beech Cellulose	Wood
Charcoal . . . . .	38.82	36.93	37.83	34.86	37.81	33.39	31.80	32.91	34.97
Tar . . . . .	4.18	4.85	11.79	6.28	8.08	9.58	7.93	5.23	8.11
Methanol . . . . .	—	Trace	0.96	0.07	0.88	—	1.60	0.19	2.07
Acetic acid . . . . .	1.39	2.18	3.50	2.79	3.19	3.89	7.08	3.50	6.04
Methane . . . . .	0.27	0.27	0.59	0.22	0.62	0.47	0.54	0.39	0.47

TABLE XXXI  
VACUUM DISTILLATION OF WOOD, CELLULOSE AND LIGNIN

Amount Used in g	Pure Charcoal	Total Distillate Per Cent	Gas and Loss	Water-soluble Residue	Alkali-soluble Residue	Water-insoluble Residue	Alkali-insoluble Residue	Ether-soluble Residue	Part in N/10 NaOH	Calc. as Acetic Acid	Total Consumption of the Water, Extraction of the Steam Volatile Distillate in N/10 NaOH	Alkali-soluble Water, Extraction of the Steam Volatile Distillate in N/10 NaOH	Consumption of the Water, Extraction of the Steam Volatile Distillate in N/10 NaOH
Cellulose . . . . .	59.4	160	71.9	12.1	43.5	1.7	0.8	—	957	470	2.8	—	—
" . . . . .	61.5	138	75.4	10.8	42.8	—	—	—	—	—	—	—	—
" . . . . .	33.8	14.8	76.9	8.3	—	—	—	—	—	—	—	—	—
Extracted pine wood . . . . .	151.4	20.4	59.6	20.0	20.5	5.5	0.2	1.397	1013*	6.1	8.2	—	—
Extracted beech wood . . . . .	145.5	26.2	63.7	10.1	21.2	5.0	—	1580	1363	8.2	—	—	—
Lignin (commercial) . . . . .	123.1	51.5	29.6	18.9	1.6	10.3	—	568	146	0.9	—	—	—
Pine lignin (laboratory) . . . . .	64.8	46.7	43.7	9.6	22	8.8	—	—	—	—	—	—	—

does not correspond with the results obtained by Klason at atmospheric pressure. It does correspond, however, with the results obtained by Hawley,<sup>20</sup> who reports an unusually high yield of charcoal in distilling a partly hydrolyzed wood, i.e., one from which the cellulose had been partly removed.

The "water-soluble dry residue" is very high from the cellulose, very low from the lignin, and intermediate from the wood. This material apparently consisted largely of levoglucosan in the case of the cellulose and wood distillates. Although the pure compound could not be isolated, yet by polarization, it was determined that the yield of levoglucosan from cellulose was about 15.8 per cent and from birch wood about 8.8 per cent.

The "alkali-soluble water-insoluble" figures represent approximately the phenol constituents of the distillates and it is interesting to note the high value for wood and lignin and the low value for the cellulose. This corresponds with the hypothesis that these aromatic compounds must have their origin mostly in the lignin and with the fact that most of the phenols are methyl ethers and that the methoxyl groups for their formation occur in the lignin.

In the case of all the products, except the acid products shown in the last three columns, the values for the products from the wood lie, as might be expected, between those from the cellulose and those from the lignin. Especially in the case of the volatile acids shown in the last column, the yields from the wood are much higher than from either the cellulose or lignin and Fischer and Tropsch attempt to explain this by assuming that the lignin distilled had suffered a loss of acetyl groups during the process of isolation from the wood. This assumption is not necessary, however, because the acetic acid in the wood-distillation products may come largely from the pentosans which are present in the original wood, but to only a slight extent in commercial paper pulp, and not at all in lignin. This explanation of the high volatile acid yield from the wood is further borne out by the work of Klason showing higher yields of volatile acid from hardwood cellulose than from softwood cellulose (see p. 203). This point could be readily proven by distilling a wood cellulose isolated by the Cross and Bevan method and therefore containing a maximum quantity of pentosans.

Although these distillations were made at reduced pressure, yet the results for acetic acid can be applied to distillation at atmospheric pressure, since Klason has shown that both acetic acid and methanol are primary products not appreciably influenced by ordinary variations in conditions of distillation. In this work the methanol was not determined, so that we have no actual direct proof of its origin in the lignin, but all the other evidence points to that source.

Heuser and Scherer<sup>21</sup> have distilled xylan and found that it gave only 7-8 per cent of acetic acid, which is not enough to account for the greater yield from wood than from cellulose and isolated lignin. They believe, however, that it is still possible that the pentosans as they exist in wood may be the precursors of the acetic acid obtained by destructive distillation.

Hawley and Aiyar<sup>22</sup> have shown in some detail the distribution of the methoxyl groups among the various crude distillation products. They assume that methane is produced entirely from the methoxyl groups in the original wood and by analyzing the liquid and solid products for methoxyl and the gas for methane, they account for about two-thirds of the methoxyl. These figures are shown in the first, fifth and eleventh columns of Table XXXII. The rest of the methoxyl is probably in the charcoal in compounds so inert that the analytical reagent does not attack it. That there is methoxyl in charcoal produced at ordinary wood distillation temperatures of 400° C. is shown by the presence of methane<sup>23</sup> and methanol<sup>24</sup> in the products obtained by heating this charcoal to higher temperatures. With these data in mind, we can proceed to a discussion of the probable source of the distillation products.

The acetic acid comes partly from the cellulose and partly from the lignin, but only a small proportion comes from a partly purified cellulose (minus most of the pentosans) or from a lignin isolated by hydrolysis of the cellulose. Probably most of the acetic acid comes from pentosans removed in the preparation of paper pulp and a part from acetyl groups which are lost in the isolation of the lignin, although there is no direct evidence of the latter source. The formic acid probably comes from the pentosans also, although the lack of determinations of this acid in most of the experimental work makes such a conclusion insecure.

The methoxyl groups in the lignin are the source of the methanol, although only a variable part of them go to make up this product. This points to a difference in the method of attachment of a part of the methoxyl groups, but there is no information available on the details of this difference. Ritter<sup>25</sup> has shown that only a part of the methoxyl is found in the isolated lignin and he has even indicated a rough relationship between the amount of methoxyl *not* found in the lignin and that which can be obtained by destructive distillation. Unfortunately in the destructive distillations of isolated lignin, the methanol yield has not been determined so this indication has not been checked. The lignin in solution in soda pulp liquors is said to yield as much methanol on destructive

<sup>21</sup> *Brennstoffchemie*, 4, 24 (1923).

<sup>22</sup> *Ioc cit*.

<sup>23</sup> "Om Trakolning," p. 180.

<sup>24</sup> Hawley, *Ind. Eng. Chem.*, 15, 697 (1923).

<sup>25</sup> *Ind. Eng. Chem.*, 15, 1264 (1923).

TABLE XXXII  
DISTRIBUTION OF METHOXYL IN PRODUCTS OF WOOD DISTILLATION  
(All figures in percentages of dry weight of wood distilled)

Products	Blank	Hard Maple		White Oak		Incense Cedar	
		(6.09 Per Cent OCH <sub>3</sub> )	Na <sub>2</sub> CO <sub>3</sub>	(5.12 Per Cent OCH <sub>3</sub> )	Na <sub>2</sub> CO <sub>3</sub>	(5.9 Per Cent OCH <sub>3</sub> )	Na <sub>2</sub> CO <sub>3</sub>
Pyroligneous acid (tar free)	1.62	1.73	1.92	1.91	1.16	1.61	1.84
Dissolved tar	0.34	0.23	0.21	0.22	0.21	0.16	0.11
Settled tar	0.52	0.60	0.59	0.46	0.56	0.60	0.12
Charcoal	0.28	0.06	0.04	0.04	0.70	0.52	0.13
Gas (calc from CH <sub>4</sub> )	1.31	1.23	1.47	1.34	1.34	0.90	0.78
Total methoxyl recovered	4.07	3.85	4.23	4.10	3.88	3.80	3.51
					2.87	3.13	2.60
						4.16	3.70

distillation as would have been obtained from the original wood, but this fact cannot be used for comparison here since this lignin is distilled in the presence of alkali and may therefore give an abnormally high yield of methanol. (See next section.)

The alkali-soluble constituents of the tar, which are largely phenol methyl ethers, come largely from the lignin.

The pentosans are obviously the source of the furfural and other furane products. Heuser and Scherer<sup>26</sup> found 12-13 per cent furfural on distilling xylan.

The charcoal and gas come from both the cellulose and lignin, although the methane in the gas and the methoxyl in the charcoal are due to the lignin only.

### Decomposition in the Presence of Chemicals

The fact that large proportions, about two-thirds, of the methoxyl groups are not recovered as methanol in the ordinary distillation of wood and that under certain conditions (see Chapter 5, Part IV) as much as 15 per cent of acetic acid could be obtained from wood led to a study of the effect of the presence of certain chemicals on the yields of methanol and acetic acid. Bassett<sup>27</sup> reported that Fremy had obtained acetone by distilling wood with 8 parts lime and in an endeavor to make the process more practical Bassett reduced the proportion of lime to  $2\frac{1}{2}$  parts. Under these conditions he claimed to obtain 26 per cent of mixed ketones mostly acetone. Schorger<sup>28</sup> later showed that Fremy had not used wood but only sugar and starch, and that Bassett's high yields were probably due to faulty analytical methods. Schorger found a maximum of 2.19 per cent acetone from three species of wood distilled with 4 parts lime.

Palmer<sup>29</sup> was the first to work with small quantities of the "catalyzers" and to make more complete determinations of the products. He worked especially with phosphoric acid and found that maple chips impregnated with 7.6 per cent phosphoric acid gave a considerable increase in methanol, but none in acid. Beech wood treated with 4.8 to 9.7 per cent phosphoric acid gave increases in both methanol and acetic acid. Perhaps the most striking effect of phosphoric acid was on the tar yields. The presence of as little as 2.7 per cent phosphoric acid reduced the dissolved tar to about  $\frac{1}{10}$  and destroyed the settled tar almost entirely.

Hawley<sup>30</sup> later tried the effect of several other chemicals and found that as little as 0.5 per cent of sodium carbonate in oak wood and 1.5 per cent in maple wood gave large increases (100 per cent and 60 per

<sup>26</sup> *Loc. cit.*

<sup>27</sup> *Chem. Met. Eng.*, **20**, 190 (1919)

<sup>28</sup> *Ind. Eng. Chem.*, **17**, 944 (1925)

<sup>29</sup> *J. Ind. Eng. Chem.*, **10**, 264 (1918)

<sup>30</sup> *J. Ind. Eng. Chem.*, **14**, 43 (1922).

cent respectively) in the yield of methanol without appreciably affecting the yields of acetic acid. Other mild alkalis had similar effects, but all the other chemicals tried gave decreased yields of both methanol and acetic acid. In order to obtain the maximum effect of the sodium carbonate, the wood must be completely impregnated and the best results are obtained by soaking sawdust in a solution of proper concentration. When oak and maple blocks 6 inches long were soaked in a solution of sodium carbonate, dried, and distilled, increases in methanol of only 16 per cent and 9 per cent respectively were obtained and when similar blocks were more completely impregnated with the solution by using 100 pounds pressure the increases were 50 per cent and 25 per cent respectively.

Similar work has recently been done on Japanese hardwoods and soft woods.<sup>31</sup> Five per cent  $\text{KNO}_3$  increased the yield of methanol from fir wood by 50 per cent and 5 per cent  $(\text{NH}_4)_2\text{CO}_3$  by 70 per cent. Sodium carbonate and  $\text{H}_3\text{PO}_4$  gave effects on methanol similar to those reported by Palmer and Hawley. The acid yields are not reported in the abstract of this paper.

The effect of phosphoric acid and sodium carbonate on the distribution of the methoxyl groups was studied by Hawley and Aiyar<sup>32</sup> in an attempt to account for the increases in methanol. Their results are summarized in Table XXXII.

The increase in methanol due to sodium carbonate is accompanied by a corresponding decrease of the methoxyl in the charcoal, dissolved tar, and gas in the case of incense cedar and oak woods. The increase in methanol due to phosphoric acid is accompanied by losses of methoxyl in all the products, the sum of which losses is greater than the gain in methanol. No hypothesis has yet been advanced to account for these effects of chemicals on the decomposition of wood by heat.

### Influence of Extraneous Substances

Since the extraneous substances are sometimes important constituents of wood and are given special treatment in Chapter 5 Part II, it may be desirable to discuss briefly the effect of their presence on the products of wood distillation. In the case of longleaf pine wood, there is an industry which destructively distills the wood and obtains valuable products whose origin is largely in the resin. Longleaf pine wood is naturally very resinous and by selecting old stumpwood and "lightwood" commercial quantities of wood containing 22-24 per cent resin can be obtained. When such wood is distilled, the volatile portions of the resin, the

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<sup>32</sup> *Loc. cit.*

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<sup>29</sup> *J. Ind. Eng. Chem.*, **10**, 264 (1918)

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<sup>31</sup> Miura, *J. Chem. Ind. Japan*, **27**, 34 (1924).

<sup>32</sup> *Loc. cit.*

turpentine and pine oil, pass over more or less unchanged according to the temperature control while the non-volatile portion, the rosin, is decomposed into volatile products. The products of distillation of the resin being oils (largely hydrocarbons) mix with the tar formed from the wood and the very complex mixture known as pine tar is the result.

There is also another industry using resinous longleaf pine wood as a raw material which recovers the resin by steam distillation and extraction without decomposing the wood. This process, however, bears no relation to the decomposition of wood by heat and therefore will not be discussed. Further details of these two industries can be found in Monograph No. 13 on Wood Distillation.

It has also been reported that another wood furnishes unusual products on destructive distillation. Although ordinary wood tar contains many of the higher phenols, especially in the form of methyl ethers, redwood tar contains phenol and cresol in sufficient quantity so that they may be separated in pure form as commercial products.<sup>33</sup> These unusual products are undoubtedly formed from the water-soluble tannin-like material in redwood<sup>34</sup> since the stumpwood which is high in extractives is said to be the preferred raw material for the process and since there is no other known difference in chemical composition of redwood which would account for these products.

Aside from these two species, there is nothing definite known about the effect of extractives on the products of wood distillation. In general it would be expected that any extractive would volatilize or decompose and add its products to those normally formed from the wood. It is sometimes stated that certain woods give low yields of methanol or acetic acid because they contain resin or tannin, implying that the extractives have an effect on the yield of products normally obtained from the wood, but there is no evidence that this is the case.

<sup>33</sup> Hund, U. S. Patent 1,365,407 (Jan. 11, 1921)

<sup>34</sup> See Part II, Chapter 5

## Chapter 3

### The Hydrolysis of Wood

The hydrolysis of wood has<sup>1</sup> been studied mainly from the standpoint of the formation of fermentable sugars and the final commercial production of ethyl alcohol. Many details of operation for obtaining the best yields have been worked out and satisfactory commercial processes have been developed without, however, obtaining sufficient detailed information on which to base a comprehensive theory of the mechanism of the reaction. In this chapter the attempt will be made to develop the subject from another point of view. Starting with what we know of the chemical composition of wood, we shall attempt to work out the details of the hydrolysis of the different constituents. This method may not be entirely satisfactory, but it is necessary in order to point out just where our information is lacking and where the future research should be directed.

#### Hydrolysis of Cotton Cellulose by Dilute Acids

As an introduction to the subject, the hydrolysis of pure cotton cellulose will be discussed briefly.

The only figures we have on the very mild hydrolysis of cotton cellulose are those obtained by the standard determinations of "corrected hydrolysis number." This determination gives a measure of the amount of hydrolysis obtained on boiling with 5 per cent sulfuric acid for 15 minutes, expressed in grams Cu reduced per 100 grams of cellulose. The corrected hydrolysis number of several samples of purified cotton averaged about 3.0<sup>1</sup> which corresponds to about 15 per cent reducing sugars formed. With increasing concentrations of acid or increasing temperatures (hydrolysis under pressure) or increasing periods of time more and more cellulose can be hydrolyzed, but the hydrolysis is only partial with dilute acids at atmospheric pressure, and the sugar formed when high concentrations or temperatures are used is partly decomposed. Wohl and Blumrich<sup>2</sup> have made some quantitative determinations of the hydrolysis of cotton cellulose with ½ per cent and 3 per cent HCl at

<sup>1</sup> Report of Cellulose Committee of the Cellulose Division of the Amer. Chem. Soc., *Ind. Eng. Chem.*, 15, 748 (1923).

<sup>2</sup> *Z. angew. Chem.*, 34, 7 (1921).

100° C. The results are shown in Table XXXIII expressed in percentage of sugars formed, computed from the original figures of grams Cu per 100 grams cellulose by dividing by the factor 2.

TABLE XXXIII  
HYDROLYSIS OF COTTON CELLULOSE WITH DILUTE ACID  
Per Cent Sugars Formed

Hours	$\frac{1}{2}$ Per Cent HCl	3 Per Cent HCl
1	—	1.55
2	0.77	3.42
4	—	4.78
6	1.38	5.43
12	2.52	7.50
20	4.75	—

They did not give corresponding figures on the loss in weight of the cellulose, but probably no appreciable decomposition of sugar took place under these conditions. It was mentioned that after the solution was separated from the remaining cellulose, further boiling increased its reducing value, thus indicating the presence of a compound intermediate between cellulose and glucose.

When the hydrolysis is carried out at higher temperatures (under pressures greater than atmospheric) the hydrolysis is greater even in less time and lower concentration of acid. Simonson<sup>3</sup> obtained the following maximum amounts of reducing sugars when treating cellulose with varying concentrations of sulfuric acid and at varying pressures:

TABLE XXXIV  
MAXIMUM YIELD OF SUGARS FROM THE HYDROLYSIS OF CELLULOSE AT VARIOUS CONCENTRATIONS AND PRESSURES

Parts Acid per 100 Parts Cellulose	Atmospheres	Pressure at Which Maximum Sugars Were Obtained	Maximum Reducing Sugars in Per Cent of Theoretical
4	.....	12	38.4
8	.	9	43.1
12	.	8	43.9
16	.	6	45.0

All the cooks were carried on for the same length of time (1 hour) and when pressures were used either higher or lower than those shown in the table, smaller amounts of sugar were obtained showing that the sugars were finally decomposed faster than they were formed when higher pressures were used. It was also admitted that the "reducing

<sup>3</sup>Z. angew. Chem., 10, 219 (1898)

sugars" formed were probably not all sugars, but that other reducing substances were probably present. There are some other interesting observations in regard to the condition of the residual cellulose, but this is all the information needed here for comparison with the hydrolysis of wood and<sup>4</sup> wood cellulose by dilute acids.

### Hydrolysis of Cotton Cellulose by Concentrated Acids

By using concentrated acids under carefully controlled conditions, a nearly complete hydrolysis of cellulose to *d*-glucose can be obtained. The reaction is not a simple one, however, several intermediate products being obtained. According to Heuser<sup>4</sup> the action of concentrated sulfuric acid on cellulose takes place in four steps:

1. The formation of cellulose dextrin.
2. The formation of sulfates of the dextrin.
3. The saponification of the sulfates.
4. The further hydrolysis of the regenerated dextrin.

It will not be necessary to go into the details of these reactions since all that is required here is a basis for comparison with a similar reaction on wood. It is sufficient to note that these four steps may all be in progress at one time, that the isolation of any one of the intermediate products in pure form may be very difficult, and that experimental data on the subject are very few.

Willstätter and Zechmeister<sup>5</sup> have followed the hydrolysis of cotton cellulose in 41 per cent HCl polarimetrically and noted a break in the curve at about the third hour, while Sherrard and Froehlke<sup>6</sup> noted another decided break (constant value for the rotation of the solution) between 6½ and 7½ hours. These sudden changes in the rate of change of the rotation indicate compounds intermediate between the original cellulose and final glucose, but no definite conclusions can be drawn as to what type of compounds or to what extent they are formed. Evidently, however, a cellulose dextrin is one of the first products formed as in the case of the action of concentrated sulfuric acid.

The hydrolysis of cellulose by either concentrated sulfuric or hydrochloric acids can be accomplished more rapidly by diluting the concentrated solutions after about three hours, and boiling the diluted solution to complete the hydrolysis. After the first step, i.e., the formation of the dextrin, the rest of the hydrolysis can be accomplished by dilute acids and under conditions which do not decompose the glucose as it is formed.

<sup>4</sup> "Lehrbuch der Cellulose Chemie," 2nd Ed., English translation, p. 138.

<sup>5</sup> *Ber.*, **46**, 2401 (1913).

<sup>6</sup> *J. Am. Chem. Soc.*, **45**, 1729 (1923).

Wohl and Krull<sup>7</sup> have shown the effect of different conditions on the amount of sugar formed by the hydrolysis, first with 41 per cent HCl at low temperatures and then by dilution and boiling. Table XXXV shows the effect of the temperature of the first hydrolysis. Ten parts of concentrated acid were used to one part of cellulose in the primary hydrolysis.

TABLE XXXV  
HYDROLYSIS OF CELLULOSE WITH 41 PER CENT HCl

Temperature of the primary hydrolysis . . . . .	0°	20°	40° C.
Duration of the primary hydrolysis . . . . .	48 hrs.	5 hrs.	5 hrs.
Carbohydrate concentration during second hydrolysis . . . . .	10%	10%	10%
Acid concentration during second hydrolysis . . . . .	1%	1%	1%
Sugar after dilution . . . . .	20.36%	24.24%	—
Sugar after boiling for 5 hours . . . . .	83.15%	99.56%	—
Sugar after boiling for 8 hours . . . . .	93.49%	108.14%	91.80%
Residue . . . . .	11.34%	3.22%	2.34%

The percentage figures for sugar are based on the weight of the cellulose taken and the figure 108.14 per cent is, therefore, 97.3 per cent of the theoretical figure for the yield of dextrose from cellulose (since 1 gram of cellulose gives rise theoretically to 1.11 grams dextrose). In fact, if the residue of 3.22 per cent is taken into consideration, the figure is slightly higher than the maximum theoretical yield. These figures show that the best temperature for the primary hydrolysis is about 20° C. These figures and others show that the best period for the secondary hydrolysis is about 8 hours, 12-hour periods decreasing the sugar yields in all cases. The acid concentration and the cellulose concentration during the secondary hydrolysis also have considerable effect, more than 1 per cent HCl and more than 10 per cent cellulose giving decreased sugar yields. The wetting of the cellulose with two to three times its weight of water before bringing it in contact with the concentrated acid was beneficial. It was also noted that the lower yields of sugar due to high concentration of acid during the secondary hydrolysis were accompanied by lower fermentation efficiency, indicating that part of the reducing material was not fermentable.

Since neither the determination of total reducing sugars nor of the rotation is a satisfactory measure of the amount of pure glucose, Momer-Wilham<sup>8</sup> isolated and weighed the pure crystallized glucose formed by the hydrolysis of cellulose. He hydrolyzed the cellulose for one week in 72 per cent sulfuric acid at room temperature, then diluted to less than 1 per cent and boiled for 15 hours. By copper reduction and polarimetric methods the yields of glucose were respectively 94.4 and 94.7

<sup>7</sup> *Cellulosechemie*, II, 1 (1921).

<sup>8</sup> *J. Chem. Soc.*, 119, 803 (1921).

per cent of the theoretical, but only 90.67 per cent pure glucose could be obtained in crystalline form.

### Hydrolysis of Wood Cellulose by Dilute Acid

It has already been pointed out in Chapter 1, Part II, that the crude wood cellulose isolated by the chlorination method is not the same as cotton cellulose, since it contains variable amounts of pentosans, mannans and glucosans. Its hydrolysis, therefore, is different from that of cotton cellulose both in the ease with which it can be effected (in part) and in the products formed. It has recently been reported<sup>9</sup> that the cellulose isolated from wood by the Cross and Bevan analytical procedure can be hydrolyzed with boiling water to a variable extent, depending on the conditions under which it is prepared. The maximum hydrolysis seems to be obtained with samples of Cross and Bevan cellulose which have been dried with some acetic or sulfuric acid still absorbed in them,<sup>10</sup> and in one case where the acid was neutralized with ammonia before drying, the loss in weight of the cellulose, due to hydrolysis, was only 4 per cent as compared with a maximum of 27.6 per cent.

This hydrolysis is, therefore, apparently a two-stage process starting with the residue from the chlorination process without drying (1) some unknown transformation taking place during drying, and (2) hydrolysis to a water-soluble material by boiling with water. The first step is not the main one, since simple washing with large quantities of hot water does not remove appreciable quantities of the cellulose and the second step is not a main one, since without the drying or the acid, only small amounts of water-soluble material are formed on boiling. Starting with the polysaccharides as they occur in the original wood, the production of this water-soluble material takes place in three stages, the first of which is the chlorination, since the drying and boiling of wood without preliminary chlorination produces no hydrolysis of the crude cellulose.

The water-soluble material obtained from isolated wood cellulose by this method is not a simple sugar or a mixture of simple sugars (monosaccharides) since its reducing value is increased about fivefold by hydrolysis with dilute acid. It also gives no test for mannose until after hydrolysis. It is made up approximately of 30 per cent mannose, 20 per cent pentose, and the rest probably glucose. Not enough work has yet been done to make possible any conclusions as to the exact composition and character of this material, but from the standpoint of the hydrolysis of isolated cellulose, it is enough to know that there is such an inter-

<sup>9</sup> Sherrard and Blanco, *Ind. Eng. Chem.*, **15**, 1166 (1923).

<sup>10</sup> Ritter, *Ind. Eng. Chem.*, **16**, 947 (1924).

mediate product in the course of the hydrolysis to simple sugars. That there was some such intermediate product has been indicated before by the fact that after partial hydrolysis of wood cellulose with dilute acids, the reducing value<sup>11</sup> of the solution was increased by further boiling in the presence of acid, but the intermediate material was never isolated.

Only a little other work has been done on the hydrolysis of isolated wood cellulose with dilute acids. In developing a method for determining the hydrolysis number of isolated wood cellulose, Hawley and Fleck<sup>12</sup> treated parts of the same sample of crude cellulose isolated by the chlorination method by boiling with different concentrations of sulfuric acid for three hours. The loss in weight of the cellulose and the reducing value of the solution were both determined. Up to a concentration of 12 per cent acid, the amount of reducing sugars corresponded fairly well to the loss in weight of cellulose but beyond that concentration the sugars were decomposed almost as fast as formed. There was no decided break in the curve showing the relation between the concentration of acid and the loss in weight of cellulose.

Mannose was not determined in those experiments, but from the work of Schorger,<sup>14</sup> it is probable that all the mannan was hydrolyzed when more than 5 per cent acid was used. Schorger found that all the mannan was hydrolyzed from wood by boiling with five per cent HCl for three and one-half hours and we would expect the isolated wood cellulose to be hydrolyzed even more readily than the original wood.

Pentosans were determined in the residual cellulose and although they were rapidly removed at the start, yet even after 50 per cent of the original cellulose had been hydrolyzed, the residue still contained three per cent of pentosans.

The difference in the hydrolysis of cotton cellulose and isolated wood cellulose by dilute acids at atmospheric pressure is seen to be very great, the latter hydrolyzing much more readily, all of the mannan and a large part of the pentosan being removed with ease. There is also a glucosan portion of the crude wood cellulose which is more readily hydrolyzed than any corresponding part of the cotton cellulose. This is shown by the glucose present in that portion of isolated wood cellulose hydrolyzed by hot water.

Sherrard and Blanco<sup>15</sup> have also given a few figures on the hydrolysis of isolated wood celluloses under high pressure and correspondingly high temperature. By treating with 5 per cent HCl at 115 pounds steam pressure for 20 minutes, they obtained an average of 25 per cent reducing sugars from the Cross and Bevan cellulose from three species of

<sup>11</sup> Paper presented at the Baltimore meeting of the Am. Chem. Soc., April, 1925.

<sup>12</sup> *J. Ind. Eng. Chem.*, **9**, 748 (1917).

<sup>13</sup> *J. Am. Chem. Soc.*, **45**, 1008 (1923).

wood. For a direct comparison, they also cooked pure cotton under exactly the same conditions and obtained only 7.49 per cent of sugar. Here again the easier hydrolysis of the isolated wood cellulose is clearly shown. It is interesting to note that hydrolysis under these conditions gives very nearly the same amount of sugars as were obtained by refluxing with 5 per cent HCl for six hours at ordinary pressure.

### Hydrolysis of Wood Cellulose by Concentrated Acids

There is apparently much less difference between the hydrolysis of Cross and Bevan wood cellulose and that of cotton cellulose when concentrated acid is used than when dilute acid is used. The conditions are such that the more resistant cotton cellulose is completely hydrolyzed and the more easily hydrolyzed portions of the wood cellulose are without much effect except that in some cases they seem to hydrolyze a little faster. Sherrard and Froehlke<sup>14</sup> have followed the hydrolysis of cotton cellulose and Cross and Bevan celluloses from wood in 41 per cent HCl by determining the rotation of the solutions at intervals until the reaction was complete and they found very little difference. Cross and Bevan cellulose from spruce (*Picea canadensis*) gave a curve almost identical to that of cotton, while a similar cellulose from a hardwood, birch (*Betula lutea*), gave the same general kind of a curve with two breaks in it, but the hydrolysis was more rapid. A similar cellulose from Douglas fir (*Pseudotsuga taxifolia*) gave a curve intermediate between those of the spruce and the birch. These differences may, however, be due more to the differences in rotation of the various sugars formed than to differences in the speed of the hydrolysis.

Heuser and Aiyar<sup>15</sup> have reported the hydrolysis of a wood cellulose by 72 per cent H<sub>2</sub>SO<sub>4</sub>. Their wood cellulose had been repeatedly extracted with caustic soda until it contained no more mannan and only about 3 per cent pentosan, so that its hydrolysis resembled that of cotton cellulose and gave almost theoretical yields of dextrose.

### Hydrolysis of Wood by Dilute Acids

We have not sufficient data on the hydrolysis of the various carbohydrate components of wood so that we can foretell just what will happen when wood is hydrolyzed and what information we have on the isolated cellulose from wood cannot be directly applied to wood as a whole since there is an evident change in properties during isolation (see p. 215 for change in cellulose during chlorination and drying). There are also two other factors which complicate the problem, (1) the

<sup>14</sup>J. Am. Chem. Soc., 45, 1729 (1922).

<sup>15</sup>Z. angew. Chem., 37, 27 (1924).

presence of lignin and other materials which may hinder the hydrolysis by mechanical protection and (2) the presence of carbohydrates in the wood which are not a part of the crude cellulose.

There is not much information available on the subject of hydrolysis of wood by water alone, but a few isolated facts may be of interest. There is in all woods a small amount of water-soluble material, a part of which may be carbohydrate<sup>16</sup> and this would give a result similar to hydrolysis, viz., a sugar in solution. It has also been noted<sup>17</sup> that the so-called "hot-water-soluble" determined in the ordinary analysis of wood is regularly greater in amount than the "cold-water-soluble" although sufficient water is used in determining the cold-water-soluble material to dissolve much more if it were actually soluble. The hot-water-soluble is also different in composition from the cold-water-soluble and the solution can be concentrated to one-quarter its original volume without throwing anything out of solution, indicating that a part of the hot-water-soluble is changed from its composition in the wood, probably by hydrolysis, as a result of boiling with water.

Boiling wood in water also forms traces of acetic acid<sup>18</sup>. In confirmation of this is the statement<sup>19</sup> that heating wet wood at temperatures far below the destructive distillation point gives 0.6 per cent volatile acids and traces of methanol. There are, however, no quantitative determinations of sugars formed by merely boiling wood with water at atmospheric pressure.

Sherrard and Blanco<sup>20</sup> have determined the reducing material formed by digesting spruce wood (*Picea canadensis*) with water at 115 pounds pressure for 15 minutes. They found 4.45 per cent and 5.48 per cent of reducing material and when the residues were recooked with acid, the sugars formed were 17.61 per cent and 18.16 per cent, respectively, giving totals about the same as would have been obtained if the wood had been cooked with acid originally. The composition of the reducing material obtained with water alone was not determined, but it was evidently a part of that obtained by hydrolysis with acid.

When wood is hydrolyzed with boiling dilute acids at ordinary atmospheric pressure considerably more decomposition is effected and there are a few quantitative data, but not a complete series. For instance, Schorger<sup>21</sup> found that mannose was completely removed from wood by boiling with 5 per cent HCl for three and one-half hours, but he did

<sup>16</sup> R. G. Smith, *Phytopathology*, **14**, 114 (1924).

<sup>17</sup> Hawley, Fleck and Richards, *Ind Eng Chem.*, **15**, 699 (1924).

<sup>18</sup> Forest Products Lab., Tech Note No. 155, and Bergstrom, *Papierfabr.*, **11**, 305 (1913).

<sup>19</sup> Hawley and Palmer, Dept Agr Bull 129.

<sup>20</sup> *Ind Eng Chem.*, **15**, 611 (1923).

<sup>21</sup> *J Ind Eng Chem.*, **9**, 748 (1917).

not determine how much of other sugars was formed. Sherrard and Blanco<sup>22</sup> found 19.85 per cent of total reducing sugars formed on boiling spruce wood (*Picea canadensis*) with 5 per cent HCl for six hours and 46 per cent of these sugars were mannose. Apparently similar results can be obtained by boiling either at atmospheric pressure or at higher pressures, provided a longer period of time and a slightly more concentrated acid are used at atmospheric pressure—that is, the effect of time and acid concentration can be made to balance the effect of temperature.

Miller and Swanson<sup>23</sup> have recently reported a series of hydrolyses of spruce wood (*Picea canadensis*) by low concentrations of hydrochloric acid with determinations of the amount of sugars formed and of Cross and Bevan cellulose removed. Their results are shown in Table XXXVI.

TABLE XXXVI  
HYDROLYSIS OF SPRUCE WOOD BY DILUTE HYDROCHLORIC ACID  
(All figures except acid concentration in percentage of original wood)

Concen- tra- tion of HCl	Loss in Weight of Wood on Hydrolysis	Reducing Sugar Formed During Hydrolysis	Reducing Sugar After Rehydrol- ysis	Cellulose in Residue by Cross and Bevan Method	Cellulose Loss on Hydrolysis
Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
0.05	9.88	2.31	6.59	51.18 *	7.70
0.10	12.72	3.50	8.57	50.96	7.92
0.15	14.67	4.54	12.07	50.08	8.80
0.25	14.75	7.32	13.15	50.89	7.99
0.50	18.33	12.52	16.28	49.00	9.82
0.75	20.13	16.15	19.00	48.31	10.57
1.00	20.16	16.37	18.05	48.61	10.27
1.50	18.78	14.12	17.34 †	48.74	10.14
2.00	19.28	15.24	17.48 †	48.62	10.26
2.50	20.17	16.37	18.67	48.79	10.09
3.00	20.95	17.54	19.40	48.70	10.18

\* The original wood contained 58.88 per cent Cross and Bevan cellulose and 28.55 per cent lignin.

† These rehydrolyses were performed with 1.5 and 2.0 per cent HCl, while the others were carried out with 3 per cent.

This table shows that with as little as 0.05 per cent HCl at 96° C. for six hours, the hydrolysis of the cellulose was very marked and the sugar formed was less than the equivalent of cellulose removed. As the concentration of acid was increased to 0.15 and 0.20 per cent, the amount of sugar formed continued to increase faster than the amount of cellulose decreased, indicating that the polysaccharides other than those in the cellulose (probably "pentosans not in the cellulose") were being hydrolyzed. It would commonly be expected that these pentosans would

hydrolyze more rapidly than any part of the Cross and Bevan cellulose, but this is apparently not the case. Finally, when 0.75 per cent acid is reached, the amount of sugar and residual cellulose reach constant values and remain constant even when the concentration of acid has reached 3.0 per cent. The final sugar value is greater than the equivalent of cellulose removed, again indicating the formation of sugars from material not in the Cross and Bevan cellulose.

According to these figures, about 10 per cent of the wood or 17.4 per cent of the cellulose is much more readily hydrolyzed than the remainder. The third and fourth columns of Table XXXVI not only indicate the presence of an intermediate compound in the hydrolysis of wood cellulose to simple sugars (as mentioned on p. 215) but also indicate that the carbohydrates *not* in the cellulose form a similar intermediate compound of lower reducing value since the difference between the figures in the two columns is greatest at .10 to .25 per cent acid where the amount of loss of cellulose is the least. It would be very interesting to have this series of hydrolyses repeated with determinations of pentosans in the wood and in the cellulose after each hydrolysis and of pentoses and mannose in the sugars after each rehydrolysis.

When we come to describe the hydrolysis of wood with dilute acid at high pressure, the picture cannot be drawn in detail—there are not sufficient data. From what we have already seen of the composition of wood and the behavior of different components on hydrolysis, several different reactions can be expected:

(1) The formation of acetic and formic acid from the acetyl groups in the lignin as shown by the "acetic acid by hydrolysis" determination in the analysis of wood.

(2) The formation of a small amount of methanol by splitting off methoxyl groups.

(3) The hydrolysis to glucose of any starch present in the wood or to the corresponding sugar or sugars of any other extractives in the wood such as gums or tannins which give sugars on hydrolysis.

(4) The hydrolysis to pentoses of the pentosans which are not a part of the crude cellulose separated by chlorination and which might therefore be expected to be the next most readily hydrolyzed carbohydrates in the wood after the starch.

(5) The hydrolysis of the hemicelluloses to the corresponding sugars.

(6) A partial attack on the resistant cellulose (i.e., the cellulose residue similar to cotton) the amount depending on the time, acid concentration, and temperature.

Superposed on these reactions there is a set of secondary reactions:

(a) The decomposition of pentoses by the acid giving furfural and formic acid.

(b) The decomposition of the hexoses by the acid giving acetic and formic acids and other products.

These primary and secondary reactions will be discussed in order. Most of the data are taken from the two papers of Sherrard and Blanco already cited<sup>24</sup>.

(1) The average yield of acetic and formic acid from five cooks on white spruce wood with 1.8 per cent  $H_2SO_4$ , at 115 pounds pressure, and for 15 minutes was 1.54 per cent and 0.37 per cent respectively. The decrease in the amount of "acetic acid by hydrolysis" in the hydrolyzed residue, in comparison with another sample of the same wood was only 1.20 per cent (from 1.32 per cent to 0.12 per cent), showing that a part of these acids comes from some other source. Cross<sup>24</sup> has shown that the acetic and formic acids obtained by boiling wood with 2½ per cent  $H_2SO_4$ , as in the analytical determination come from the lignin, probably from acetyl and formyl groups and these groups are almost completely removed by the pressure hydrolysis. The source of the rest of the acetic and formic acid will be discussed in a later section.

Kressmann<sup>25</sup> has determined the amount of acetic and formic acids formed by the hydrolysis of several species of wood under the same conditions. His yields for white spruce (*Picea canadensis*) run a little higher than Sherrard's. The principal interesting point in this collection of figures is that the hardwoods give generally much higher yields of acetic acid and a higher ratio of acetic to formic. These higher yields of acetic acid from hardwoods correspond with the higher "acetic acid by hydrolysis" as determined by analysis, but here again the latter figures are not high enough to account for all the acetic acid formed on pressure hydrolysis. The variation in the formic acid between hardwoods and softwoods is not explainable from present information.

(2) The methoxyl in spruce wood was decreased by hydrolysis from 4.75 per cent to 3.99 per cent. It was not determined whether the amount of methanol formed was equivalent to the decrease in methoxyl but this was probably the case since Heuser and Schmelz<sup>26</sup> have shown that the methoxyl in lignin can be almost quantitatively transformed into methanol by treatment with hydrochloric acid under pressure. The small amount of methoxyl removed by 1.8 per cent  $H_2SO_4$ , at 115 pounds pressure apparently corresponds with that readily hydrolyzed portion of the methoxyl that is removed during the procedure for the analytical separation of lignin.<sup>27</sup> Sherrard and Blanco call attention to the fact that although the amount of lignin has not been decreased by hydrolysis, yet the methoxyl has been decreased and they consider this an indication.

<sup>24</sup> Dissertation, Gottingen (1910).

<sup>25</sup> Dept. Agr. Bull., 983, p. 48.

<sup>26</sup> *Celluloschemie*, I, 49 (1920).

<sup>27</sup> Ritter, *Ind. Eng. Chem.*, 15, 1264 (1923).

that a part of the methoxyl is not attached to the lignin. This conclusion is not necessarily indicated because the amount of lignin in the original wood was determined by a method which also split off a part of the methoxyl from the lignin as it occurred in the original wood. The same line of reasoning could be as well applied to the "acetic acid by hydrolysis."

(3) The question of the amount of sugar formed from starch during the hydrolysis of wood has never been investigated, in fact the amount of starch present in various species and kinds of wood has never been determined (see p. 39). However, any starch present will undoubtedly be readily hydrolyzed to sugar and probably more easily and quickly than any other carbohydrate in the wood.

In the same group belong gums such as the galactan which occurs in western larch (*Larix occidentalis*). This is very readily hydrolyzed and increases in corresponding amount the sugars formed by any given hydrolytic treatment.<sup>28</sup> There are probably other gum extractives like this which give sugars on hydrolysis, but their effects have not been studied. Tannins and glucosides may even give a small amount of glucose on hydrolysis, but this has never been considered in connection with the hydrolysis of wood.

(4) Much the same condition prevails in regard to the pentosans in the wood which are not a part of the Cross and Bevan cellulose, except that we have good figures for the amounts of those present in different species. Undoubtedly they are among the first components hydrolyzed, but no study has been made of their hydrolysis and their presence is commonly ignored when hydrolysis is discussed. Ritter and Fleck<sup>29</sup> have shown that roughly one-third of the pentosans in hardwood and one-half of those in softwoods are not found in the cellulose isolated by the chlorination method. Sherrard and Blanco<sup>30</sup> have shown that in spruce wood the total pentosans are reduced by hydrolysis from 10.76 per cent to 1.79 per cent while the "pentosans in cellulose" on the same basis are reduced from 4.53 per cent to 0.95 per cent. The pentosans *not* in the cellulose are, therefore, reduced from 6.23 per cent to 0.84 per cent and probably the equivalent amount of pentoses is formed. The hydrolysis of this part of the pentosans will be discussed further in the next section in connection with the other carbohydrates, but it should be noted here that we have no data, except those of Table XXXVI, which show that they are hydrolyzed before or at the same time as the other carbohydrates. It would be a very simple matter to determine these points by a few mild hydrolyses with determination of

<sup>28</sup> Kressmann, Dept. Agr. Bull. 983, and Sherrard, *Ind Eng Chem.*, **14**, 948 (1922).

<sup>29</sup> *Ind. Eng. Chem.*, **14**, 1050 (1922)

<sup>30</sup> *Loc. cit.*

the amounts of pentoses formed and the amount of "pentosans not in the cellulose" remaining.

(5) We have seen that the Cross and Bevan cellulose isolated from wood contains certain portions that are more readily hydrolyzed than other portions of the wood cellulose or than cotton cellulose. There is a little doubt as to whether the same constituents, as present in the original wood, hydrolyze just as readily (see p. 218) but it is certain that they still hydrolyze more readily than cotton cellulose. There are no complete figures as to just the order in which the various sugars are formed, but the complex isolated by Sherrard and Blanco (see p. 215) indicates that considerable portions of the mannose, pentose, and glucose are formed at the same time. The variation in the composition of the complex, however, makes it impossible to compute any satisfactory figures for the exact proportions of those sugars simultaneously formed. The only general statement that can be made on the order of the hydrolysis of the different sugars is that there is no experimental evidence of one sugar being formed in advance of the others. It is very desirable that someone make a series of partial hydrolyses of wood with complete analyses of the residue and of the hydrolysate. Sherrard and Blanco have made these complete analyses for one hydrolysis only and their results have been of great value in developing this chapter.

Galactose has been frequently identified among the sugars from the hydrolysis of wood but, except in the case of western larch wood where a water-soluble galactan is known to be present, the exact source of the galactose is not known. Since water-soluble galactans have not been found in the other species, the galactose probably results from the hydrolysis of the cell wall constituents along with the mannose and pentoses.

There is no sharp dividing line between the hydrolysis of the hemicelluloses and that of the residual cellulose. This is to be expected from the fact that cotton cellulose even shows some hydrolysis under the conditions required for a complete hydrolysis of the hemicelluloses (see Table XXX).

(a) The decomposition of the primary products of hydrolysis of the wood, the simple sugars, is important since it takes place under the conditions required for the maximum sugar formation. It is to be expected that the pentoses would be partly decomposed to furfural under the conditions of moderate hydrolysis. When spruce wood (*Picea canadensis*) is cooked at 115 pounds pressure with 1.8 per cent acid for 15 minutes, 3.71 per cent furfural is formed on the average and this is equivalent to 5.10 per cent pentosans, and still another portion may be decomposed to give formic acid as shown by Kfessmann.<sup>31</sup> This

<sup>31</sup> U. S. Dept. of Agr. Bull. 983, p. 31.

shows that a considerable portion of the pentosans may form other products than pentoses during hydrolysis.

(b) Glucose is also decomposed under the conditions of its formation by hydrolysis as shown by many series of hydrolysis of wood or cellulose under conditions of gradually increasing severity until finally the glucose is decomposed faster than it is formed. Neuman<sup>32</sup> has made a detailed study of the amount of decomposition of glucose at different temperatures and acid concentrations and as a result placed the "critical point" at 175° C. above which temperature the hydrolysis of cellulose to glucose should not be attempted on account of rapid decomposition of glucose. Sherrard and Gauger<sup>33</sup> have shown that mannose decomposes at about the same rate as does glucose. The rate of decomposition of galactose under similar conditions is not known, but this sugar is comparatively unimportant in amount.

It is evident from the data of many investigators that there is a maximum amount of sugars which can be formed by the hydrolysis of a given wood and that within certain limits variations in the time, temperature or acid concentration do not have much effect on this maximum. And yet, there is always a residue of cellulose left unhydrolyzed after this maximum is reached. The favorite explanations for these facts are (1) that the residue of unhydrolyzed cellulose has been changed to a more resistant form which withstands further hydrolysis and (2) that an equilibrium is finally reached with increasing severity of treatment or with increasing amounts of sugar in solution, where the decomposition of the sugars is as rapid as their formation. Both these explanations may have a value but the first is not well supported by experimental data and the second requires additions in order to explain all the facts in regard to the yields of sugars from different cellulosic materials.

TABLE XXXVII  
REPEATED HYDROLYSES OF THE SAME WOOD

Number of Hydrolysis	Conditions of Hydrolysis	Sugar, Per Cent	Estimated Cellulose Present	Per Cent Sugar on Cellulose Present
1	HCl for 1 hour at 100° C.	18.3	55	33.8
2	H <sub>2</sub> SO <sub>4</sub> for 15 minutes at 170° C.	13.1	39	33.5
3	H <sub>2</sub> SO <sub>4</sub> for 15 minutes at 170° C.	7.4	27	" 27.4
4	H <sub>2</sub> SO <sub>4</sub> for 15 minutes at 170° C.	5.4	20	27.0

<sup>32</sup> Dissertation, Dresden (1910), p. 31, also reported by Kressmann, *loc. cit.*

<sup>33</sup> *Ind. Eng. Chem.*, 15, 1164 (1923).

It has been shown by Neuman that wood or cellulose can be repeatedly hydrolyzed under the same conditions and continue to yield sugar on each hydrolysis. His data are not sufficiently complete to determine accurately whether the residual cellulose hydrolyzes as readily as the original, but by a few assumptions and calculations some light can be thrown on the subject. His data are shown in the first three columns of Table XXXVII. In column 4 are the estimated amounts of cellulose present figured from the amounts of cellulose probably removed by the preceding hydrolyses. In the first hydrolysis, it is assumed that a part of the sugar comes from non-cellulose constituents, as was found to be the case during the discussion on p. 219. After the first hydrolysis, the loss in cellulose was assumed to be a little greater than the equivalent of the sugar formed in order to allow for the decomposition of a small part of the sugar. These calculations are rough and it cannot be expected that the results are accurate, but they make it possible to compute the approximate percentage of sugar formed on the basis of the cellulose present at the beginning of each hydrolysis. Such computations, shown in column 5, indicate that the ease of hydrolysis of the cellulose has not been affected to any great extent by repeated hydrolyses especially when we consider the probable protective action of the increasing proportion of non-cellulose material present after each hydrolysis.

Direct comparisons cannot be made between the first and second hydrolyses because they were not made under the same conditions and because the first had the chance to act on the more readily hydrolyzed constituents of the wood, while the second had mostly the residue of nearly pure cellulose for its raw material. With the same conditions of acid concentration, temperature and time for the first and second hydrolyses, we would expect a higher percentage of sugar formed (on the basis of the cellulose present) during the first hydrolysis on account of the presence of these easily hydrolyzed materials.

An explanation of the low maximum yields of sugar obtainable by one hydrolysis which assumes a modified and highly resistant residual cellulose cannot be accepted although it is true that there is present in wood a mixture of various readily hydrolyzed constituents which are first removed, leaving a residue of cellulose which is normally more resistant to hydrolysis. This residue, however, is still hydrolyzable under the same conditions used in obtaining the maximum sugar yields and some other explanation must be sought for the occurrence of this maximum while considerable cellulose still is present.

Keeping in mind this readily hydrolyzable portion of the cellulose, let us examine the second explanation for the fact that less than theoretical yields of sugar are obtained, i.e. that with increasing severity of hydrolysis a point is finally reached where the sugars are decomposed

faster than they are formed. It has already been shown (p. 223) that glucose and mannose may be decomposed under the conditions required for moderate hydrolysis. It has also been shown that the pentoses decompose even more rapidly than the hexoses since with increasing severity of hydrolysis a point is reached where *total* sugars do not increase but fermentable sugars do increase.<sup>34</sup> Sherrard and Gauger<sup>35</sup> have reported some figures on the apparent decomposition of sugars during the actual hydrolysis of wood under increasing acid concentrations which are especially interesting since they show the amount of cellulose hydrolyzed in every case. Their results are shown in Table XXXVIII. With 5 per cent acid, the amount of sugars found are much less than the equivalent of the cellulose removed showing a considerable decomposition of sugars even aside from the "pentosans not in the cellulose" (see p. 215) which must have been largely decomposed also. With the next higher concentration of acid, 10 per cent, the total sugars are about the same, but the fermentable sugars have increased showing the formation of more hexoses, but the decomposition of more pentoses. Here again 11 per cent cellulose has been removed with the addition of only 2 per cent to the hexose sugars. At the next higher concentration of acid, 15 per cent, both total and fermentable sugars are reduced although 7 per cent more cellulose is removed and this continues with increasing concentrations until finally, although nearly all the cellulose has been removed, yet only a very small amount of sugar is left undecomposed.

In the same article, these authors have shown similar figures for gradually increasing temperatures and periods of hydrolysis which show similar maxima of total and fermentable sugars, but unfortunately they did not determine the amount of cellulose remaining after these hydrolyses.

TABLE XXXVIII

HYDROLYSIS OF WOOD WITH INCREASING CONCENTRATIONS OF SULFURIC ACID  
(All figures in percentages of original dry wood)

Grams of $H_2SO_4$ per 100 of Dry Wood	Total Reducing Sugars	Fermentable Sugars	Cellulose Unchanged	Cellulose Removed
5	21.98	16.29	31.70	26.50
10	21.54	18.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20.	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

It would seem, therefore, that the mechanism of the hydrolysis of the carbohydrate portion of wood with about 1.8 per cent  $H_2SO_4$  and 115 pounds pressure is somewhat as follows: First, the most readily

<sup>34</sup> Kressmann, *loc. cit.*, p. 35.<sup>35</sup> *Ind. Eng. Chem.*, 15, 1164 (1923).

hydrolyzable portion of the Cross and Bevan cellulose (about 13 per cent according to Miller and Swanson) is attacked, then the carbohydrates not a part of the cellulose, along with the rest of the easily hydrolyzable part of the cellulose (about 4.7 per cent more) and finally the residue of pure cellulose. In the first two parts of this attack, intermediate compounds are formed, but under the conditions of hydrolysis assumed here, they do not last long but are rapidly converted into the simple sugars. Under these conditions also, the three steps mentioned are not well defined but occur almost simultaneously. At the same time a part of the sugars are decomposed, the pentoses more rapidly than the hexoses. With slightly less severe conditions, less sugar is decomposed, but less is formed, while with slightly more severe conditions, although more sugar is formed, more is decomposed and the total sugars remaining are about the same. The only marked effect of variations in conditions is to influence the ratio of pentose to hexose sugars, although the more severe conditions may give slightly lower yields of *total* sugars due to the more rapid decomposition of the pentoses.

It may be concluded, therefore, that the maximum yield of sugar will be determined largely by the amount and composition of readily hydrolyzed materials present, the relation of the total sugar yield to the amount of readily hydrolyzed material being governed by the decomposition of the sugar under the conditions of formation.

It is admitted that there are not sufficient data to make this conclusion absolutely sure, but it is the best that can be offered until further experimental work is done. Further evidence in its favor is the work of Sherrard on the hydrolysis of western larch.<sup>36</sup> The wood with which he worked contained water-soluble galactan sufficient to form 10.11 per cent reducing sugar on extraction with water and subsequent hydrolysis. The extracted wood gave 19.64 per cent sugar when hydrolyzed for 15 minutes at 115 pounds pressure and with 1.8 per cent sulfuric acid. When unextracted wood was hydrolyzed under the same conditions except at 107 pounds pressure, 29.0 per cent sugar was obtained. Thus the total sugar is increased by very nearly the exact amount of additional easily hydrolyzed material present.

#### Effect of Catalysts

Since the maximum yields from a given material are controlled by the equilibrium between the reactions of sugar formation and sugar decomposition, it seemed possible to hasten the former or retard the latter or both and thus obtain higher yields. Sherrard and Gauger<sup>37</sup> have tried many catalysts in an attempt to accomplish this, with positive but

<sup>36</sup> *Ind. Eng. Chem.*, 14, 948 (1922).

<sup>37</sup> *Ibid.*, 15, 63 and 1164 (1923).

small effects. Some of their most marked effects both favorable and unfavorable are shown in Table XXXIX.

These results were all obtained by adding the catalyst to the 2.5 per cent  $H_2SO_4$  and cooking at 115 pounds pressure for 15 minutes. Certain of the catalysts increased the sugar yields slightly, but it is not known whether this was due to hastening the hydrolysis or retarding the sugar decomposition, since no analyses were made of the amount of cellulose left in the hydrolyzed wood. Other of the catalysts reduced the sugar yield very much and most of these also reduced the proportion of fermentable sugars, although this last effect may have been due to a chemical effect on the yeast rather than to an actual influence on the proportion of sugars present which would be fermentable in the absence of the catalyst.

TABLE XXXIX  
EFFECT OF CATALYZERS

Catalyst	Total Reducing Sugars, Per Cent	Per Cent Fermentable
None .....	21.14	66.0
1.25 per cent $MgSO_4$ .....	22.14	64.4
0.50 per cent $CoSO_4$ .....	22.37	66.2
0.50 per cent $Fe_2(SO_4)_3$ .....	22.37	65.6
1.25 per cent $ZnSO_4$ .....	20.06	65.2
1.25 per cent $CoSO_4$ .....	22.11	70.1
OK		
0.50 per cent $C_{10}H_8 <$	23.17	67.8
COOK		
OK		
1.25 per cent $C_{10}H_8 <$	23.03	67.7
COOK		
1.25 per cent $K_2Al_2(SO_4)_4$ .....	18.99	48.4
1.00 per cent $UO_2(NO_3)_2$ .....	15.94	68.6
2.00 per cent $H_2O_2$ .....	19.42	64.6
1.00 per cent $H_2O_2$ .....	17.68	52.6
1.00 per cent $FeCl_3$ .....	15.18	59.4
0.50 per cent $CoO_2$ .....	14.82	54.2
1.25 per cent $Na_2S$ .....	7.46	24.9

In the previous discussion little has been said in regard to the effect of different acids, since it has been assumed that the hydrolytic action was controlled only by the hydrogen ion concentration of the acid used. This is probably true except as some other part of the acid may exert a catalytic effect on the hydrolysis. Sherrard and Gauger found this to be the case with oxalic acid and benzenesulfonic acids which gave higher yields of sugar than corresponding concentrations of sulfuric acid. On the other hand, such highly dissociated acids as formic and tri-chlor acetic gave very low sugar yields.

### The Hydrolysis of Different Species of Wood

Kressmann hydrolyzed many different species of wood under identical conditions and determined total and fermentable sugars. The main differences found were between the hardwoods and the softwoods, the softwoods, for instance, giving between 20.02 and 23.61 total sugars with between 66.5 and 77.6 per cent of the total sugars fermentable, and the hardwoods between 16.60 and 21.24 per cent total sugars with between 22.22 and 47.22 per cent fermentable. These figures do not include western larch (*Larix occidentalis*) which on account of the large amount of galactan present gave unusually high total sugars and an unusually low proportion of fermentable sugars.<sup>38</sup> There are no analytical figures available for these species which indicate a relationship between chemical composition and sugar yields, except the higher percentage of pentosans in the hardwoods which would account for the higher proportion of unfermentable sugars and perhaps also for the lower total sugars (on account of the more rapid decomposition of the pentoses).

The differences in total sugars among the softwoods are probably due to differences in the amount of readily hydrolyzable material in the original woods and the variations in proportion of fermentable sugars are probably due to variation in the amount of pentosans present. The latter conclusion has some data to confirm it, although the analyses and hydrolyses were not made on the same samples of wood. Table XL shows Cross and Bevan cellulose, pentosan in cellulose, and total pentosan determination on four species of softwood together with total reducing sugars and percentage fermentable sugars obtained by hydrolysis under identical conditions.

TABLE XL  
RELATION BETWEEN COMPOSITION OF WOOD AND YIELDS OF SUGAR ON HYDROLYSIS

	Total Sugar, Per Cent	Per Cent Ferment- able	Pentosans in Cellulose	Total Cellulose	Total Pentosans
White spruce ( <i>Picea canadensis</i> ) .....	23.61	71.44	61.85	9.63	10.34
Longleaf pine ( <i>Pinus palustris</i> ) .....	23.16	72.90	58.48	7.71	7.46
White pine ( <i>Pinus strobus</i> ). ....	21.00	74.49	59.71	5.33	6.97
Douglas fir ( <i>Pseudotsuga taxifolia</i> ) .....	21.13	75.16	61.47	5.34	6.02

There is seen to be an inverse relationship between the amount of pentosans in the wood and the percentage of fermentable sugars and .

<sup>38</sup> Sherrard, *Ind. Eng. Chem.*, 14, 948 (1922), has since shown that the galactose can be fermented at the same time as the mannose and glucose by a proper control of the conditions. At the time of Kressmann's work the galactose was considered unfermentable.

the high yields of total sugars are also associated with the high pentosans. If there were some analyses of the woods including the "hydrolysis number" of the cellulose for comparison, some further relationships could probably be established.

In the case of the hardwoods, there is no apparent relation between composition and sugar yields. The softwoods have been studied in more detail than the hardwoods on account of the larger yields of fermentable sugars readily obtained from the former and it is possible that with hardwoods an increased severity of hydrolysis would produce a higher proportion of fermentable sugars in the total sugars, and even a higher total yield of fermentable sugars. On the other hand, if higher yields of total sugars were required regardless of the proportion of fermentable sugars, such a result could probably be obtained by less severe hydrolysis with correspondingly less decomposition of pentoses.

### Hydrolysis of Wood with Concentrated Acids

This subject has not been studied so much as the hydrolysis with dilute acids since large and nearly theoretical yields of sugars are readily obtained and its problems are the economic and engineering problems of recovery of acid and development of proper construction materials for the commercial apparatus. At one time this process was in commercial operation in Germany, but no details of operation are available except that concentrated hydrochloric acid was used and recovered by distillation at reduced pressure.

Most of the experimental data available on the action of concentrated acid on wood are given by Wohl and Krull.<sup>39</sup> Using conditions which they had previously worked out as best for cotton cellulose (except a much longer period, 20-24 hours, for the primary hydrolysis) they obtained 67 and 70 per cent reducing sugar from two samples of spruce wood. No further examination of these reducing materials was made and in two other experiments on spruce wood where fermentations were run, an average yield of only 61 per cent sugar was reported. These sugars were fermented and alcohol obtained corresponding to about 18 per cent of the weight of the original wood or only about 60 per cent of the theoretical yield if all the reducing material was dextrose. The authors explain this by a reversion to unfermentable reducing substances of a part of the dextrose first formed due to the long continued primary hydrolysis and this may account for a part of unfermentable material, but the presence of pentoses is a simpler and surer explanation of another part. If it is assumed that the spruce wood contained 10 per cent pentosans and that they were all hydrolyzed to pentoses, 11.4 per cent pentoses would be

\* *Cellulosechemie*, II, 1 (1921).

found in the 61 per cent total sugars. These would account for nearly half the unfermentable reducing material.

No analyses are given by the authors of the spruce wood they used for their hydrolysis, nor were any analyses made of the sugars aside from the fermentations, so it is difficult to discuss the subject of the relation of the composition of the wood to the products obtained. If, however, we assume 60.55 per cent yield of cellulose by the Cross and Bevan method (the authors give this figure by Renker for the kind of spruce with which they worked) and 10 per cent of total pentosans with 5 per cent in the cellulose, some interesting computations can be made. The 55.55 per cent cellulose consisting of hexose residues should give theoretically 61.1 per cent of hexose sugars and the 10 per cent pentosans (part in the cellulose and part not) should give 11.3 per cent pentose sugars or a total of 72.4 per cent reducing sugars. Of these sugars the 61.1 per cent hexoses should be fermentable with a yield of 31.2 per cent alcohol. The actual results obtained indicate the decomposition of hexose sugars equivalent to  $31.2 - 18 = 13.2$  per cent alcohol or 25.8 per cent sugar, of which 14.5 per cent still gave a reducing value and the remainder of 11.3 per cent did not. This is on the assumption that all the pentoses remained as such without decomposition.

In view of the much more nearly theoretical yields obtained from cotton cellulose, the opinion is suggested that the fermentation experiments may have been at fault. If this is not the case, then the next attempt at higher yields of alcohol should be in the direction of shorter periods for the primary hydrolysis. Even if much less of the wood cellulose were attacked during the shorter period, there might still be more fermentable sugars left on account of less decomposition.

The authors attempted to increase the yields by treating the wood in various ways, by chlorination, with caustic soda, ozone, ammonia, etc., and they succeeded in increasing the total reducing sugars by all the methods tried. Apparently, however, the alcohol yields were decreased in all cases.

The use of concentrated acids for the hydrolysis of wood certainly has a great advantage over dilute acids in the matter of alcohol yields, but the former method has several disadvantages: (1) necessity for using much greater amounts of acid which requires an acid recovery system, (2) much longer time required for the process, and (3) the use of much more expensive apparatus in order to handle the concentrated acid. In the process just described, the primary hydrolysis required 20 hours, and the secondary, 8 hours which would certainly be prohibitive in practice. However, as has been pointed out, the primary hydrolysis may perhaps be shortened without disadvantage and it seems certain that the secondary

hydrolysis could be shortened by using higher temperatures and still obtain the same results.

In cases where large amounts of very cheap wood waste are available, the dilute acid process might be preferable, but with small quantities of more expensive wood, the longer and more complicated process might be the better.

## Chapter 4

### The Delignification of Wood

The term "delignification" as used in this chapter applies only to the removal of lignin from wood, although it has previously been used to describe attacks which were supposed to result in the separation of lignin from cellulose without the solution or removal of the former.<sup>1</sup> The term has also been used to describe effects which were supposed to be, but obviously were not, due to the removal of lignin. The botanist and pathologist in studying various fungal and chemical attacks on wood by microchemical methods, have frequently reported delignification to have taken place because parts of the wood took the cellulose stain after the attack, but not before, or because certain color reactions were absent after the attack.<sup>2</sup> It has been shown that wood can be made to take the cellulose stain by purely physical changes<sup>3</sup> so that this cannot be considered an indication of the removal of lignin. Crocker<sup>4</sup> has shown that some of the color reactions of lignin are due to groups that are very readily removed without much effect on the composition of the lignin, and therefore the lack of these color reactions cannot be considered an indication of delignification. Hubert's assumption<sup>1</sup> that decay causes first a separation of lignin and cellulose, a delignification, later followed by a removal of one or the other or both components, is apparently due to the same kind of fallacious reasoning from color reactions.

Since we have so little information on the constitution of lignin, it is not to be expected that many details can be given on the chemistry of the removal of lignin from wood. In fact, the development has been in the other direction and most of the information we have on the constitution of lignin has come from observations of processes for delignification. This state of affairs is due to the fact that delignification has been developed as an analytical method for determining cellulose in wood and as commercial processes for making paper pulp from wood, this practical development taking place previous to any considerable knowledge of the

<sup>1</sup> Hubert, *J. Agr. Res.*, XXIX, 526 (1924).

<sup>2</sup> Spaulding, *Mo. Bot. Gard. Ann. Rep.*, 17, 41 (1906).

<sup>3</sup> Robinson, *Trans. Roy. Soc. London*, Series B, 210, 54 (1920).

<sup>4</sup> *J. Ind. Eng. Chem.*, 13, 625 (1921).

chemistry of wood. As in many other industrial chemical processes the *how* preceded the *why*.

There is a large amount of literature in English on the technical, commercial aspects of the pulp and paper industry and the reader is referred to this if he is interested in that part of the subject.<sup>5</sup> In this chapter only those technical subjects will be referred to which have a direct bearing on the chemistry of wood.

### Delignification by Chlorination

This subject has already been treated from the analytical standpoint in Chapter 6, Part III (and in Chapter 3, Part II) and will be included here only briefly for comparison with other methods of delignification. It is generally considered (on very meagre experimental data) that the action of chlorine on wood in the presence of water produces a lignin chloride or lignone chloride<sup>6</sup> which is not soluble in water but is rendered soluble by a water solution of sulfur dioxide or a sulfite. According to Ritter and Fleck<sup>7</sup> the action of the chlorine is at first very rapid but is soon retarded by the protection of the lignin-chlorine compound. After removing this with the sulfite solution, the chlorine again acts rapidly.

According to Cross and Bevan<sup>8</sup> in the chlorination of jute fiber, the amount of chlorine combining with the lignin is approximately the same as the amount given off in the form of HCl and this indicates that the action of the chlorine is a simple hydrogen replacement. The action of the sulfite on the lignin chloride is also said to be identical with its action on the chlorinated derivatives of pyrogallol, mairogallol and leucogallol. When wood is chlorinated, however, the reaction is more complicated. Heuser and Sieber<sup>9</sup> have shown that the amount of chlorine combining with the lignin is less than one-third the amount given off as HCl, indicating a considerable oxidation as well as a hydrogen replacement. In the case of pine wood these authors found chlorine combining to the extent of 9.5 per cent of the weight of the wood and 31.3 per cent given off as HCl.

The removal of lignin by chlorination of any one sample of wood leaves a fairly definite aggregate of carbohydrates since the conditions of the action can be varied to a considerable extent with very little effect on the amount or composition of the residue. Over-chlorination will produce a residue containing more oxidized cellulose and less alpha-cellulose

(the decrease in the latter probably being a direct result of the formation of the former), but the total amount of residue remains remarkably constant.<sup>10</sup> Under-chlorination will, of course, leave some lignin but this can usually be guarded against by the color reaction with the sulfite solution which persists as long as lignin is present.

Delignification by chlorination leaves a larger amount of carbohydrates as a residue than any of the other delignification processes and this may be one reason why it has been so largely used as an analytical method. Not all the carbohydrates of the original wood are in this residue since a large part of the pentosans go into solution during the chlorination. There is no evidence that any hexosans, except such extraneous materials as starch or galactan, also go into solution and the amount of hexoses obtained from the Cross and Bevan cellulose and from the original wood by mild hydrolysis are so nearly the same<sup>11</sup> that in most cases all the hexosans are found in the crude cellulose isolated by chlorination.

It is not known just what differences exist between the pentosans "in cellulose" and those "not in cellulose" to cause them to react differently on chlorination. It might be thought that the chlorination produces a very mild hydrolysis and that the most readily hydrolyzed pentosans were, therefore, not separated with the more stable carbohydrates, but the work of Miller and Swanson<sup>12</sup> has shown that some of the most readily hydrolyzed carbohydrates of the original wood are found in the chlorination residue. It must be, therefore, that the pentosans not found in the cellulose residue after chlorination are less strongly bound to the other carbohydrates and that they are soluble in sulfur dioxide solution or are rendered soluble by the chlorination in some way other than by hydrolysis. Much information on these suppositions could be furnished by determining whether the "pentosans not in cellulose" existed in the washings from the cellulose residue in the form of pentosans or pentoses. It is even possible that these "pentosans not in cellulose" are actually not bound to the cellulose but instead are connected more or less intimately with the lignin, giving rise to the controversy in regard to whether the pentosans sometimes found in the lignin really belong there.

#### Delignification by Acid Sulfites

The removal of lignin by acid sulfites has been the basis of the preparation of paper pulp from wood for many years. The first process developed used a solution of sulfur dioxide in water, but lime was soon added to the liquor in order to correct certain disadvantages supposed to

be due to the formation of sulfuric acid and sulfonic acids, and lime or lime and magnesia have been a part of commercial sulfite liquors ever since. Recently, however, Miller and Swanson<sup>13</sup> have found that the SO<sub>2</sub> as sulfurous acid was the main active reagent and Cross and Engelstadt<sup>14</sup> have shown that a nearly complete removal of the lignin can be obtained with sulfurous acid alone and at lower temperatures than when lime sulfite is also present. Various hypotheses have been advanced in regard to the actual chemical reactions involved and the composition of the soluble lignin compounds formed but as has been seen from the chapter on the constitution of lignin, none of these are entirely satisfactory. The fact that acid sulfites are the solvent agent has led to the belief that aldehyde groups in the lignin are somehow involved and for the same reason the formation of soluble "lignin sulfonic acids" is a very natural explanation. Since free sulfurous acid is the most important part of the "sulfite liquor" used, the reaction is sometimes considered to be largely hydrolytic. Since none of these hypotheses is complete and satisfactory and since the same subject has been discussed from the standpoint of lignin constitution in Chapters 3 and 4, Part II, no attempt will be made here to trace the main reactions of the lignin when wood is treated with sulfites. There are, however, plenty of other data for discussion in connection with this delignification.

The action of bisulfites on wood does not take place to any appreciable extent at ordinary temperatures and even at the boiling point of water the reaction is slow. With SO<sub>2</sub> alone the reaction is practically complete in about 15 hours at 100-115° C. The commercial processes using calcium and magnesium bisulfites may take from 8 to 20 hours, depending on the rate at which the temperature is raised and on the final maximum reached which is usually 140° to 155° C.

The speed of the reaction in commercial processes is limited by slowness of the penetration of the chips and the lack of complete circulation of the liquor. Miller and Swanson<sup>15</sup> working with sawdust in small apparatus and under conditions of rapid heating and pressures not obtainable in large commercial apparatus, found that the time required for the reaction was reduced approximately one-half for every 10° increase in temperature between 120° and 150° C., and that a change in sulfurous acid concentration from 1 per cent to 3 per cent also reduced the time required by about one-half. With a liquor containing 4 per cent free SO<sub>2</sub> and cooking at 150° C., they obtained a 90 per cent removal of the lignin in one and one-third hours.

gradual change from wood to pulp is given in the report of a series of experiments at the Forest Products Laboratory.<sup>16</sup> In order to obtain representative samples and known quantities of the pulp and the cooking liquor at different stages of the reaction, separate runs were made under

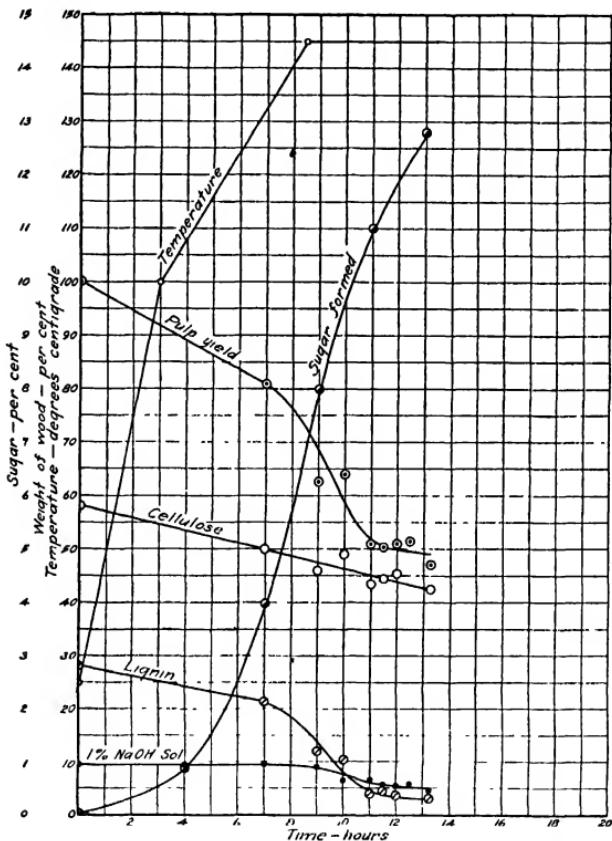


FIG. 12.—Curves Showing the Action of Sulfite Liquor on Spruce Wood.

identical conditions except that the charge was blown after different cooking periods from 7 to 13 hours. The amounts of pulp and liquor were

<sup>16</sup> Miller and Swanson, *Paper Trade J.*, **74**, No. 15, 295 (1922); Bray and Andrews, *ibid.*, **76**, No. 3, 49 (1923); Sherrard and Suhm, *J. Ind. Eng. Chem.*, **14**, 931 (1922).

then determined and samples taken for analysis. The analytical results for cellulose and lignin in the pulp and sugar in the liquor (all based on the dry weight of the original wood) are shown in Fig. 12 together with the yield figures for pulp and the temperature curve.

It is very noticeable that the cellulose was considerably decreased even during the first cooking period of 7 hours although only a small part of the lignin (even less in percentage than the cellulose) had been removed. During this period the chips were very little softened. The rate of cellulose removal remains very constant till about the eleventh hour when the reaction is practically complete. This removal of the cellulose even during the first stages of the process shows the impossibility of obtaining by the sulfite process a yield of pulp which will correspond with the amount of cellulose in the wood as determined by the chlorination method.

The removal of the cellulose is due to a hydrolysis by the free sulfurous acid forming various sugars and apparently this hydrolysis follows very much the same course and results in the same products as that produced by dilute hydrochloric or sulfuric acids (see chapter on Hydrolysis). The curve in Fig. 12 showing the amount of sugar present at different stages of the reaction does not correspond as it should with the loss in cellulose, the amount of sugar at all stages being less than would be expected even if the Cross and Bevan cellulose were assumed to be the only source of sugar. When it is considered that sugars must also be formed from the carbohydrates not a part of the Cross and Bevan cellulose, the shortage of sugars from the theoretical amount is even greater. This can be explained in two ways: (1) By the formation of polysaccharides intermediate between the cellulose and the simple sugars which are soluble (loss of cellulose) but do not give the reducing action of the simple sugars, and (2) by the decomposition of a part of the sugars formed. Both of these factors influencing the sugar yields have been shown in the previous chapter to be important in connection with the hydrolysis of wood.

The first of these is probably of most importance during the first period, since the intermediate polysaccharides are more rapidly hydrolyzed into simple sugars during the last part of the process when the temperatures are higher. This is shown by the fact that from the seventh to the eleventh hour more sugars are formed than are equivalent to the amount of cellulose removed. Five per cent cellulose is removed equivalent to about 5.6 per cent sugars, while 7 per cent sugars are formed. The decomposition of the sugars probably takes place mostly during the latter part of the cook when the temperatures are higher.

The sugars were unusually low during these cooks, probably on account of the low concentration of free  $\text{SO}_2$ , 2.39 per cent at the beginning of the cook. Another similar cook with 4.46 per cent free  $\text{SO}_2$  gave 16.3 per cent sugars. In a digestion by the "quick-cook process" a

maximum yield of 21.6 per cent sugar is reported<sup>17</sup> from spruce wood with a pulp yield of 48.8 per cent. Hägglund also says<sup>18</sup> that with a 48 to 50 per cent pulp yield it should be readily possible to obtain 16 per cent sugar and he shows<sup>19</sup> one instance of 20.5 per cent sugar from spruce wood with a pulp yield of 48.5 per cent. These higher sugar yields are rather more than would be expected if all the polysaccharides in the original wood, except those found in the pulp, had been hydrolyzed into simple sugars. Hägglund's average figure of 16 per cent sugars and 50 per cent pulp yield, however, is very close to what would be expected. If we assume that the pulp contains 48 per cent of polysaccharides and that the

16

16 per cent sugars represent  $\frac{16}{50} = 0.32$  or 32 per cent polysaccharides, then

1.11

the total polysaccharides in the original wood accounted for in these products amount to  $48 + 14.4 = 62.4$  per cent. This allows for a decomposition of part of the sugars to form furfural, acetic acid and other products thus accounting for the difference between 62.4 per cent and the total polysaccharides in the original wood.<sup>20</sup>

The final residue of pulp<sup>21</sup> in Fig. 12 is seen to contain about 4 per cent lignin and lignin is a common constituent of crude sulfite pulps. Bray and Andrews<sup>22</sup> have shown from 1.3 to 7.8 per cent in commercial crude pulps. Undoubtedly this lignin could be more completely removed under more severe cooking conditions but only at the expense of decreased quantity of cellulose and poorer quality of pulp. The chemical changes which accompany an "over-cooked" or "burned" pulp are not known but the strength and color are markedly affected. It has been found that this residual lignin, if it must be removed, can be best removed by the bleaching process which improves the color without serious effect on the strength. The chemistry of bleaching will be taken up later.

It is also noticeable from Fig. 12 that the sum of the lignin and the cellulose does not quite equal the crude pulp. It is not known in detail what this other material may be, but it is partly ash, partly "pitch" (resins or fats) and perhaps partly substances similar to the cellulose or lignin that are not separated along with these constituents in the analytical pro-

<sup>17</sup> Sherrard and Suhm, *Ind. Eng. Chem.*, 17, 194 (1925).

<sup>18</sup> *Svensk. Kem. Tids.*, 36, 133 (1924).

<sup>19</sup> *Ibid.*, 36, 284 (1924).

<sup>20</sup> We believe that Hägglund's figures of 69.7 per cent total carbohydrates in spruce wood are too high. With 28 per cent lignin this allows only 2.3 per cent for "resin, ash, protein, etc." The resin, ash and protein will commonly make up more than 2.3 per cent, leaving a minus quantity for the "etc," which is really a considerable figure in wood composition.

<sup>21</sup> The use of the word "pulp" to indicate the residue after the cooking process is recommended. Through mistranslation of the German word "Zellstoff" the word "cellulose" is frequently applied to this material.

<sup>22</sup> *Loc. cit.*

cedure. The pulps separated at the eleventh hour and beyond showed from 0.2 to 0.8 per cent hot water soluble material, from 5.3 to 5.9 per cent substances soluble in 1 per cent NaOH, and from 1.00 to 1.95 per cent ash.

The amount of material soluble in 1 per cent NaOH (corrected for the hot water soluble matter) is shown in Fig. 12. It is not known just what this consists of but it is commonly considered that a part of the lignin and a part of the pentosans are dissolved by caustic soda. This material, whatever it is, is not appreciably affected in total amount during the first nine hours' cooking but diminishes to a nearly constant value of 5 to 6 per cent at the eleventh hour and beyond. Apparently the cooking process renders some part of the wood, probably a part of the lignin, more soluble<sup>23</sup> and this counterbalances the removal of another part of the alkali-soluble, probably some of the pentosans, and makes the total the same. Finally most of the lignin is removed and the alkali soluble matter diminishes and remains constant at a point higher than the residue of lignin.

In the series of analyses plotted in Fig. 12 the determination of pentosans was not included either on the total pulp or on the cellulose so that we do not know at what rate they are removed by the cooking process. There are some figures, however, on the amount of pentosans and mannose-yielding residues in commercial sulfite pulps. Mahood and Cable<sup>24</sup> found that from a softwood containing 14 per cent pentosans an incompletely cooked sulfite pulp with a yield of 61.2 per cent of the wood contained 8.5 per cent pentosans, while a well-cooked pulp with a yield of 47.3 per cent contained 6.6 per cent. Figured on the basis of the original wood those percentages are 5.2 and 3.1, of which 4.3 per cent and 3.0 per cent, respectively, were found in the cellulose isolated from the pulp by the chlorination process. These figures show that in the first part of the sulfite cooking process, corresponding to about the ninth hour in Fig. 12, about 40 per cent of the pentosans still remain in the pulp and of these about 33 per cent were in the cellulose and 7 per cent not in the cellulose. A well-cooked pulp, corresponding to about the twelfth hour in Fig. 12, still contained 22 per cent of the pentosans of the original wood, practically all of which were found in the cellulose.

Hägglund reports<sup>25</sup> that a sulfite pulp representing 47.1 per cent of the original spruce wood contains on an average 6.1 per cent of "polysaccharides of high molecular weight" which on hydrolyses yield 2.8 per cent mannose, 2.1 per cent xylose and 1.2 per cent fructose. Sherrard and Blanco<sup>26</sup> have also reported 2.0 per cent mannose and 2.2 per cent pentoses from sulfite pulp but they did not report any fructose among the

<sup>23</sup> See chapter on Deterioration, where it is shown that a partial removal of the cellulose renders the residue more soluble in NaOH.

<sup>24</sup> *Ind. Eng. Chem.*, 14, 727 (1922).

<sup>25</sup> *Papierfabr.*, 23, 399 (1925).

<sup>26</sup> *Ind. Eng. Chem.*, 15, 611 (1923).

sugars obtained by hydrolyzing spruce. Lenze, Pleus and Müller<sup>27</sup> found mannose and xylose but made special attempts to identify fructose and galactose without success.

The methoxyl groups in the original wood are partly converted into methanol during the cooking process, but the amount is small, only a few tenths of a per cent. The rest apparently remain combined with the lignin in the liquor or in the crude pulp. Mahood and Cable<sup>28</sup> have found 1.00 per cent methoxyl in sulfite pulp but we have seen no determinations of methoxyl in the waste liquor although individual methoxyl determinations have been made on isolated ligno-sulfonates.

Acetic and formic acids are always products of the cooking of wood with sulfite liquor. Hägglund<sup>29</sup> has made a detailed study of these products and finds from 2.6 to 4.2 per cent acetic and 0.04 to 0.09 per cent formic acid on the basis of the original wood in a series of cooks under different conditions. There was no apparent relation between the conditions of the cook and the amount of acids produced, except that in general the lower pulp yields were accompanied by higher acid yields.

The acetic acid formed in these cooks is considerably more than the "acetic acid by hydrolysis" obtained by the analytical method. It is not known whether this indicates a different source for a part of the acid or simply a more complete reaction. Hägglund points out that the amount corresponds approximately to one acetyl group to one molecule of Klason's  $\alpha$ -lignin. It is also possible that a part of the acetic and formic acids may come from a decomposition of the sugars (see chapter on Hydrolysis).

Furfural is also formed probably by the decomposition of the pentoses during the latter part of the cook but only to the extent of a few tenths of a per cent of the wood.<sup>30</sup>

Whatever volatile oils are present in the wood are volatilized by the high temperatures of the cooking process and the presence of steam so that they are removed from the pulp in the "blow-off" or pressure relief from the digester. In the case of the spruce wood used largely for the sulfite process in this country, the oils recovered in this way consist largely of cymene.<sup>31</sup> The same is true of the spruce used in Sweden.<sup>32</sup> Among the higher boiling constituents of the crude "spruce turpentine" Wheeler and Harris<sup>33</sup> have recently identified l-borneol. No examination has been made of the composition of the volatile oil naturally occurring in spruce wood, so that it cannot be safely stated whether the cymene occurs in the

<sup>27</sup> *J. prakt. Chem.*, 7-9, 213 (1920-21).

<sup>28</sup> *J. Ind. Eng. Chem.*, 14, 727 (1922).

<sup>29</sup> *Svensk. Kem. Tids.*, 36, 133 (1924).

<sup>30</sup> Krause, *J. Soc. Chem. Ind.*, 29, 217 (1906).

<sup>31</sup> Schorger, *J. Ind. Eng. Chem.*, 10, 258 (1918).

<sup>32</sup> Klason, *Ber.*, 33, 2343 (1900); Bergstrom, *Papierfabr.*, 10, 359 (1912).

<sup>33</sup> *J. Elisha Mitchell Sci. Soc.*, 40, 111 (1924).

wood or is a transformation product of a terpene which occurs in the wood.

The spruce gum obtained by tapping the live tree yields a volatile oil which consists largely of alpha pinene<sup>84</sup> but since it has been shown that the volatile oil in a wood is not necessarily of the same composition as that obtained from the live tree (see Chapter 5, Part II) cymene might still be found in the wood. This is not probable, however, since terpenes are much more common than other hydrocarbons in wood resins. Aside from the volatilization of the oil, the resin is not appreciably affected and remains in the pulp.

### Waste Sulfite Liquor

In commercial sulfite-pulp processes the pulping liquor containing over half of the original wood in solution is largely a waste product. The fermentable sugars are sometimes used as a source of ethyl alcohol but the formation and composition of these sugars have already been discussed and need not be further considered here. Even this process is only a partial solution of the waste problem since the lignin products and unfermentable sugars still remain to be disposed of. A great deal of work has been done on possible methods of utilization of sulfite liquor<sup>85</sup> and such of the results as have added to our knowledge of the chemistry of the subject have already been mentioned in the chapters on Lignin and Lignin Products. Many suggested uses have been connected with simple group properties of the whole material and have not given much indication of chemical composition. Such uses include those of dust layer, briquet and core binder, tanning material, and fuel. Although a preparation from waste sulfite liquor is used commercially as a tanning material, is absorbed by the hide, and in connection with other tanning materials makes good leather, yet it is not necessarily a true tannin. The fusion of the sulfite liquor solids with caustic potash will be mentioned in the next chapter.

### Resistance to Attack by Sulfites

Since it has not been shown that there is much difference in chemical properties between various species of wood, except between the two classes of hardwoods and softwoods, it is sometimes difficult to account for the fact that many woods are resistant to delignification by sulfites. In the case of the resinous pines the explanation is not difficult, since it is known that the resin is not affected by the cooking process (except for the

<sup>84</sup> *Bull Imp Inst*, 22, 31 (1924).

<sup>85</sup> A good bibliography of the subject is found in Bull. No 66 of the Forest Products Laboratories of Canada by Johnsen and Hovey.

volatilization of the lower-boiling oils) and probably exists in sufficient amount to furnish a mechanical protection to the wood fibers. The red cedars are probably resistant for the same reason, although the properties of their resins are not so well known. Among the non-resinous woods which are difficult to pulp are chestnut, red and white oak, catalpa, black locust, and redwood but all these contain unusual amounts of tannins or tannin-like, water-soluble substances which may account for the resistance to sulfites. There are, however, several woods which are very resistant to pulping by the sulfite process but are not known to contain any considerable amount of extraneous materials which might account for the resistance. These are white pine, sugar pine, limber pine, basswood and slippery elm. The common explanation for the difficulty in pulping these woods is that there is something about their structure which prevents the penetration of the liquor into the chip but there are no known peculiarities of structure in these woods which confirm this explanation.

### Delignification by Caustic Soda

The first commercial processes of making paper pulp from wood used caustic soda for the delignifying agent but we know perhaps less about the chemistry of this process than of the later sulfite process. At least, less research work has been done and fewer hypotheses offered to explain the details of the reaction. Since the lignin solvent is a strong alkali it is natural to assume that it combines with "lignin acids" but this conception has no experimental basis, at least so far as concerns carboxyl groups in the original lignin. It is more probable that phenolic hydroxyl groups are involved in the formation of soluble phenolates. What little is known about the chemical reaction between lignin and caustic soda has been given in Chapters 3 and 4, Part II, and need not be repeated here.

The attack on the lignin by caustic soda is apparently more rapid than that by sulfites, since the process on commercial pulp chips is practically complete in three to four hours. A direct comparison of speeds is difficult because the soda process uses a higher maximum temperature of about 170° C. and the maximum temperature is usually obtained more rapidly. There are no figures available for comparison on the speed of the soda process when more finely divided wood is used, such as sawdust.

Although we may know little of the detailed chemical reactions which take place, yet we have a fairly complete picture of the result of the reactions expressed in terms of the composition of the pulp and the liquor at different stages of the process from original wood to finished pulp.<sup>55</sup>

<sup>55</sup> Wells, Grabow, Staidl and Bray, *Paper Trade J.*, **76**, No. 24, 49 (1923); Bray and Andrews, *ibid.*, **76**, No. 19, 49 (1923); S. S. Aiyar, *Ind. Eng. Chem.*, **15**, 714 (1923).

A series of cooks were made under the same conditions except that each charge was blown after a different cooking period of from one-half to seven hours. The cooking conditions were as follows:

1. Weight of chips ..... 100 pounds dry weight
2. Caustic soda ..... 20 pounds\*
3. Vol. of cooking liquor at start ..... 25 gallons
4. Time in reaching maximum temperature ..... 1 hour
5. Maximum temperature ..... 170° C.

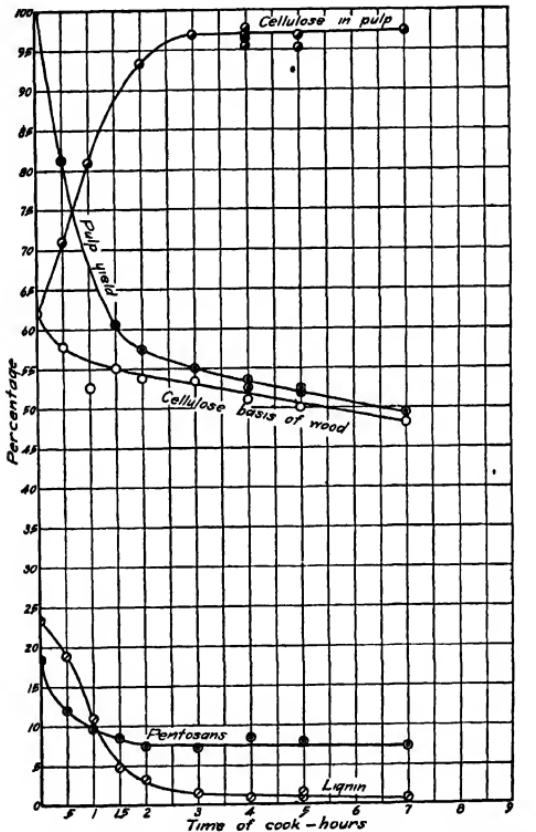


FIG. 13.—Curves Showing the Action of Soda Liquor on Aspen Wood.

Part of the results on one hardwood, aspen (*Populus tremuloides*), and one softwood, jack pine (*Pinus divaricata*), are shown in Figs. 13 and

14. The other results which are not so suitable for plotting will be given later. Here, as in the sulfite process, it is noted that the cellulose is removed most rapidly at the start of the reaction, a part of the Cross and Bevan cellulose, probably the most readily hydrolyzable part, being attacked and removed while there is considerable lignin still left in the pulp. This again points to the impossibility of obtaining yields of pulp comparable with the Cross and Bevan cellulose in the wood. The jack pine apparently has more of this unstable cellulose than the aspen, since the loss in Cross and Bevan cellulose after three hours cooking is nearly 20 per cent in the former and only about 9 per cent in the latter. Pentosans were determined only in the pulp from the aspen but here at least they seem to form a part of the stable cellulose, since they remain constant in quantity between the third and seventh hour, while the total cellulose is reduced by more than 5 per cent.

The lignin was dissolved very rapidly from the start and its removal was practically complete in three and four hours, respectively, for the aspen and pine. The higher proportion of lignin in the pine wood may account for this difference in time required. After these periods further cooking reduces the pulp yield mostly by destroying the cellulose without increasing its purity.

It was attempted to determine the lignin dissolved in the liquor by the same method as that used for the pulp, viz., by separating the material not soluble in 72 per cent sulfuric acid but the results were not consistent and in most cases more lignin had been dissolved from the wood than could be precipitated from the liquor.

The total volatile acid in the liquor reached a maximum at about one and one-half hours, the difference between the hardwood and softwood being shown in the yield of about 10 per cent from aspen and 5 per cent from jack pine. These yields are considerably higher than those obtained by destructive distillation but they are in about the same ratio. It is difficult to trace the components of the wood which furnish the volatile acids during the cooking with caustic soda. Whatever acetyl groups are present, like those which give acetic acid on hydrolysis, account for their quota of acetic acid but this is only a small part of the total. The higher pentosans in the hardwood makes it appear that the pentosans may be the main source of acetic acid. This explanation has also been used for the source of the acetic acid obtained by destructive distillation but in neither case is there any direct evidence.

The methoxyl content of the pulp from jack pine decreased rapidly during the first two hours and became nearly constant after the third hour, the methoxyl content of the liquor increasing in the same manner. In fact the methoxyl was removed at almost exactly the same rate as the lignin. The conditions in which different portions of the methoxyl were

found in the liquor were, however, different, part being volatile in the form of methanol, and part being non-volatile, probably still in combination with the lignin. Also the proportion of volatile methoxyl varied

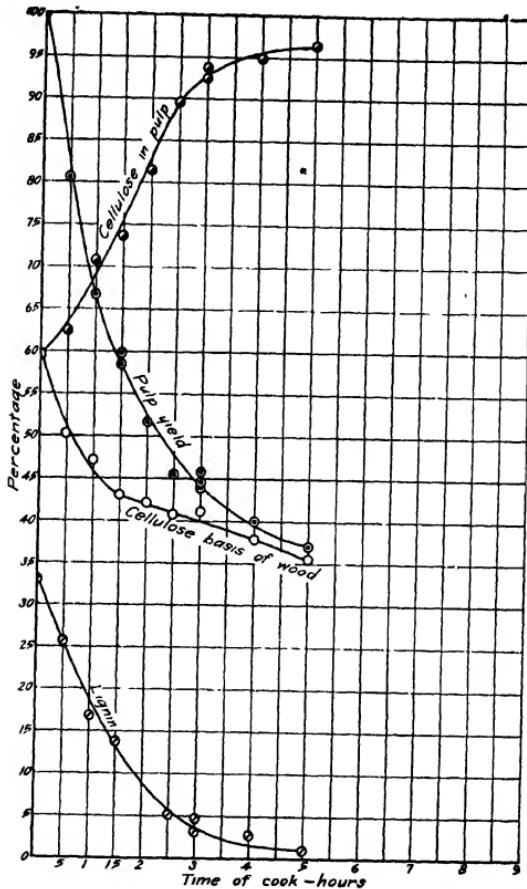


FIG. 14.—Curves Showing the Action of Soda Liquor on Jack Pine' Wood.

considerably at different periods. During the first one and one-half hours the amount of volatile methoxyl increased rapidly to about 1.5 per cent the weight of the wood and then decreased to about 1.0 per cent at the end of the third hour. Either figure is higher than the amount of methanol

which would be expected from the destructive distillation of a softwood like jack pine. It is interesting to note that the soda process of pulping wood produces more methanol and more acetic acid than the destructive distillation of the same wood.

Except for the determinations of the pentosans in the pulp, we have no figures on what becomes of the readily hydrolyzable carbohydrates during the soda process. They are probably hydrolyzed to sugars but the sugars are decomposed by the alkali at the high temperatures used. It has been suggested that a part of the volatile acids are formed during this decomposition but this reaction is certainly not quantitative and no analyses have been made of the liquors to show the other sugar decomposition products. Except for the pentosans, we do not know what readily hydrolyzed part of the cellulose is left in the pulp, such as the small mannose and glucose residues in sulfite pulp.

The resins which may be present in woods cooked by the soda process are partly dissolved (the resin acids) and partly volatilized (the volatile oils). The turpentine oils obtained from the pines in this way are apparently not changed in composition, being the same as those obtained by steam distillation. On account of this ready solubility of the resins they are no protection to the wood against the action of caustic soda and all resinous woods can be delignified by this process. In fact there seem to be no extraneous materials in wood which offer any serious resistance to penetration or cooking by the soda liquor. The resins or tannins may require the use of additional alkali but otherwise they offer no difficulties.

#### By-Products from Soda Liquor

In commercial soda-pulp processes the liquor is evaporated, calcined and causticized for the recovery of the caustic soda. In connection with the recovery process the possibility of obtaining valuable by-products has been shown. White and Rue<sup>37</sup> evaporated and destructively distilled commercial soda liquor from mixed hardwood, mostly birch, and obtained about 120 per cent of methanol and 0.018 per cent of acetone on the weight of the original wood. This is somewhat less than the amount of such products obtainable by destructive distillation of the original wood. They also obtained about 54 per cent of a tar which contained a higher proportion of oils boiling below 270° C. than the ordinary hardwood tar. The acetic acid in the liquor is not recovered either as acid or acetone by this process but is apparently decomposed into methane by distillation in the presence of excess alkali.

A more recent method has been designed to utilize potentially the acetic acid also.<sup>38</sup> This is accomplished by mixing the concentrated soda

<sup>37</sup> *Met. Chem. Eng.*, 16, 82 (1917), and *Paper*, 19, 56 (1917).

<sup>38</sup> V. Drewsen, U. S. Patents 1,298,479 and 1,248,480.

liquor with lime before distillation. In this way the acetic acid is largely converted into acetone. There are no available detailed figures on this process but it is claimed that in a large-sized experimental apparatus there were obtained not only more alcohol but acetone more than equivalent to the acetic acid from the destructive distillation of the original wood. This seems to be perfectly possible since it has been shown that more acetic acid is formed during the cooking of wood by the soda process than by the destructive distillation of the same kind of wood.

### The Sulfate Process

Delignification by the so-called "sulfate" process is a modification of the soda process in which sodium sulfide as well as caustic soda is present. It is called the "sulfate" process because sodium sulfate is added to the liquor to replace losses but this is reduced to sulfide in the recovery process. The effect of the sulfide on the chemical reaction is not known because we do not even know the chemical reaction in the case of caustic soda alone but there are some comparative figures showing the composition of the products at different stages of the process. Wells<sup>39</sup> has carried out a series of cooks under the same conditions as those listed in connection with Fig. 14 except that two pounds of sulfur were added to the cooking liquor for each charge. This resulted in a cooking liquor of approximately the same composition as that obtained in commercial plants by the complicated reactions of the recovery process. Fig. 15 shows the results obtained on jack pine. In comparison with the soda process on the same species it is very noticeable that the removal of the lignin is much more rapid when the sulfur is present. The rate of removal of the cellulose is also much less rapid during the first half hour. It is possible, therefore, by means of the presence of sulfide to remove more lignin with a lesser attack on the cellulose.

In this set of cooks no pentosan or other determinations were made to show in what way the cellulose in the pulps differed from that in the soda pulps on account of the lesser attack of sulfur process, but it has been shown by Mahood and Cable<sup>40</sup> that a spruce soda pulp with 33.8 per cent yield contained 5.0 per cent pentosans while a similar sulfate pulp with a 39 per cent yield contained 7.1 per cent pentosans. A part of the higher yield is, therefore, due to the presence of more pentosans, but the other differences in composition to account for the rest of the higher yield are unknown.

The volatile acids in the liquor were almost the same as in the soda liquor but the maximum amount was attained even sooner. No determina-

<sup>39</sup> *Pulp Paper Mag. Can.*, 21, 623 (1923).

<sup>40</sup> *J. Ind. Eng. Chem.*, 14, 727 (1922). See Table XLV.

tions of methoxyl groups were made in this series of cooks but about 0.3 per cent methanol is formed in commercial sulfate processes along with

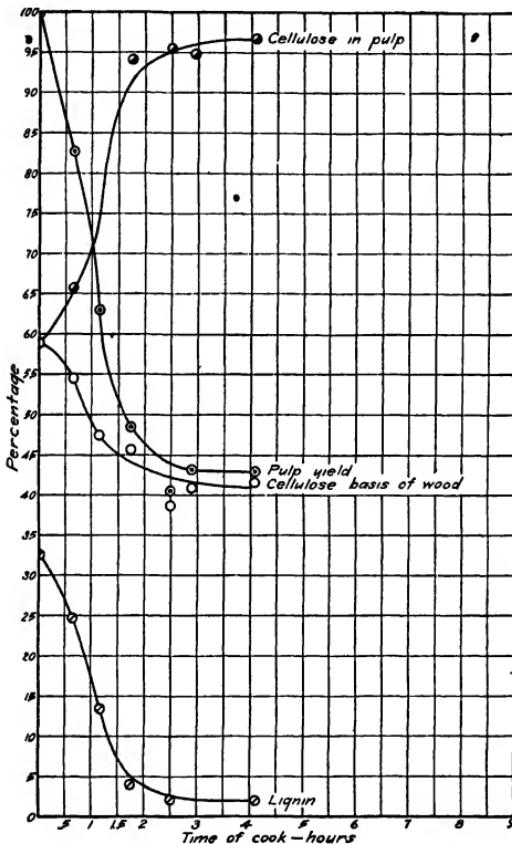


FIG. 15—Curves Showing the Action of Sulfate Liquor on Jack Pine Wood.

smaller amounts of dimethyl sulfide, methyl mercaptan, and other volatile sulfur compounds.

#### Delignification by Neutral Sulfites

Other methods of delignification have been used in the study of wood such as the use of phenols and oxidation with nitric acid and potassium chlorate. Various modifications of the sulfite and soda processes have

TABLE XII  
COOKING CONDITIONS AND ANALYSIS OF PRODUCTS IN THE TREATMENT OF ASPEN WITH SODIUM SULFITE

Cook No.	Cooking Conditions			Results of Cook			Analysis of Pulps		
	Weight of Wood Grams	Used Based Ten- on Weight of Wood	Time of Cooking Hours	Cellulose Based on Yield of Pulp			Lignin Based on Wood (loss)		
				Na <sub>2</sub> SO <sub>3</sub>	Consumed Based on Wood	Pulp Per Cent	Wood Pulp Per Cent	Wood Pulp Per Cent	Wood Pulp Per Cent
10 *	15.0813	12.8	170	4	68.73	9.0	85.89	59.03	5.53
3	14.6257	25.8	170	4	70.05	9.0	86.68	60.72	3.84
4	14.6283	51.3	170	4	68.49	11.9	87.49	59.92	4.64
5	14.6148	77.6	170	4	68.42	12.9	87.37	59.77	4.79
6	14.6250	103.3	170	4	67.79	16.0	87.47	59.30	5.26
7	14.6001	103.5	170	4	68.07	—	87.42	59.51	5.05
8	14.5907	128.9	170	4	67.63	19.7	87.60	59.24	5.32

\* Pulp was slightly burned.

TABLE XLII  
COOKING CONDITIONS AND ANALYSIS OF PRODUCTS IN THE TREATMENT OF ASPEN WITH SODIUM SULFITE  
Time and chemical approximately constant

Cook No.	Cooking Conditions			Results of Cook			Analysis of Pulps		
	Used Based Weight on Weight of Wood	Temp- erature ° C.	Time of Cooking Hours	Na <sub>2</sub> SO <sub>3</sub> , Consumed Based on Wood			Cellulose Based on Wood		
				Pulp	Wood (change)	Pulp	Wood	Pulp	Wood
19	14.7139	54.3	120	4	90.20	0.7	73.32	66.13	+ 1.57
13	14.7880	54.3	130	4	87.03	0.6	76.67	66.72	+ 2.16
39	15.1301	52.5	130	4	87.29	1.6	66.91	67.13	+ 2.57
12	15.0987	53.5	140	4	84.25	3.6	78.15	65.84	+ 1.28
11	15.0872	53.5	150	4	80.55	6.2	79.83	64.30	- 0.26
32	15.1333	51.5	150	4	80.35	5.0	79.68	64.02	- 0.54
20	14.7225	54.3	160	4	76.78	7.4	80.66	61.93	- 2.63
4	14.6283	51.3	170	4	68.49	11.9	87.49	59.92	- 4.64
38	15.1337	50.6	170	4	69.22	11.3	87.88	60.83	- 3.73
29	15.1471	50.9	180	4	59.39	18.4	93.17	55.33	- 9.23
30	15.1520	51.1	185	4	57.37	19.7	94.07	53.96	- 10.60
31	15.1342	52.1	185	6	50.29	28.7	96.80	48.68	- 15.88
43	15.1045	50.6	185	8	48.69	33.7	95.50	46.49	- 18.07

+ indicates increase or gain. — indicates decrease or loss.

been suggested, such as the addition of various neutral salts and the use of neutral sulfites.<sup>41</sup> None of these has become of any importance from the analytical or commercial standpoints and only one has developed any new information on the mechanism of delignification.

There are some actual chemical data<sup>42</sup> in connection with the use of neutral sodium sulfite for delignification which show that it reacts somewhat differently from the other delignifying agents. Since this is a new field in which details are not readily available, the complete cooking and analytical data will be given. The work was carried out on aspen sawdust between 40 and 60 mesh which had been previously extracted with benzene and alcohol, the extracted wood containing 64.56 per cent Cross and Bevan cellulose and 21.83 per cent lignin. Tables XLI and XLII show two series of cooks, in the first of which temperature and time were kept constant and the concentration of  $\text{Na}_2\text{SO}_3$  varied, and in the second, time and concentration were constant (except for the last two cooks) and temperature varied. Table XLIII gives a series of soda cooks on the same wood for comparison.

In Table XLI it is seen that under the temperature and time conditions the cellulose remains high and nearly constant with changing concentration of sulfite while the lignin is reduced from 21.83 per cent in the original wood to about 9 per cent with low concentrations of sulfite and finally to 5.2 per cent with the high concentrations. This is truly remarkable delignification (or partial delignification) since next to the chlorination process it leaves by far the largest amount of crude cellulose unattacked. But the limit of the removal of the lignin is apparently reached at this point, at least in so far as it can be effected by reasonable concentrations of sulfite. Unfortunately, no results are reported with the same temperature but a longer time of cooking which might possibly have reduced the lignin further and still without more attack on the cellulose. When an attempt was made to remove more lignin by raising the temperature (see Table XLII) the cellulose was rapidly attacked and finally the cellulose yields are lower than those from the soda process, although the most severe cooking with sodium sulfite never gave less than a 3 per cent residue of lignin.

It is interesting to note that in the first part of Table XLII where very mild cooking conditions were used, there was an apparent increase in Cross and Bevan cellulose, in one instance an increase of 2.57 per cent more than was present in the wood. Here is another case, similar to the apparent increase of lignin on bleaching soda pulps,<sup>43</sup> where our analytical

TABLE XLIII  
COOKING CONDITIONS AND ANALYSIS OF PRODUCTS IN THE TREATMENT OF ASPEN WITH CAUSTIC SODA

Cook No.	Cooking Conditions				Results of Cook				Analysis of Pulps			
	NaOH Used	Tem- pera- ture on Weight of Wood	Time of Cooking of Pulp	Yield	Cellulose Based on		Lignin Based on		Wood (loss)	Wood	Wood	Per Cent
					NaOH Consumed	Based on Wood	Wood	Pulp				
17	15.0992	32.59	170	0.5	59.29	13.8	85.98	50.44	14.12	12.39	7.34	14.49
16	15.1067	32.57	170	1.0	52.30	16.2	97.24	50.85	13.71	2.77	1.45	20.38
18	15.1140	32.55	170	2.0	49.39	19.2	99.40	49.09	15.47	0.63	0.31	21.52
15	15.0930	32.60	170	3.0	47.10	21.5	99.65	46.93	17.63	0.21	0.10	21.73
41	14.8475	16.85	180	2.0	57.20	16.0	93.77	53.65	10.85	9.00	5.14	17.13
21	14.7310	16.97	170	2.0	58.89	14.6	91.44	53.84	10.72	8.77	5.16	16.67
22	14.7405	16.96	160	2.0	63.40	13.1	86.70	54.96	9.60	13.22	8.38	13.45
23	14.8897	16.79	150	2.0	68.02	12.0	82.66	56.22	8.34	17.54	11.93	9.90
24	15.1450	16.50	140	2.0	71.53	11.6	78.64	56.25	8.31	21.02	15.03	.680

Note. Cook No 41 was made with a sample of wood analyzing: Cellulose, 64.50 per cent; Lignin, 22.27 per cent.

methods are not accurate. Something which was not cellulose in the original wood has been so transformed that it isolated along with the cellulose by chlorination. With more severe cooking the apparent excess of cellulose disappears but there is no way of telling whether the material which caused the excess disappears or whether it remains and a part of the original cellulose goes into solution. There is an indication that the latter is the case, that the false cellulose persists in the pulp and that at least a part of it is determined as lignin also. In each of the last four cooks of Table XLII, the sum of the lignin and cellulose in the pulp is more than 102 per cent. This indication, however, is not confirmed in Table XLI because here none of the pulps run much over 100 per cent cellulose plus lignin. A study of the material might furnish some valuable information on the chemistry of wood.

Further study of the neutral sulfite process is desirable, especially more complete analyses of the pulps and the cellulose isolated from the pulps. At present it is not possible to decide in what way the cellulose in the pulp varies in composition from that in ordinary pulps as it must vary in order to account for the high yields. A few pentosan determinations would probably have thrown considerable light on this question.

No extended study of species has been made by the neutral sulfite process but it seems to be especially well adapted to the hardwoods. It also seems well adapted for semi-pulping processes<sup>44</sup> in which only enough lignin is removed (the middle lamella lignin) to slightly soften the chips so that the fibers can be subsequently loosened by mechanical means. Since so little cellulose is dissolved by this process, the final yields of pulp are very high, 75 to 80 per cent. On account of the large amounts of lignin in such a pulp, it cannot be readily bleached but fortunately several woods give a light-colored pulp without bleaching.

### Properties and Composition of Wood Pulps

The quality of a wood pulp is commonly determined by various mechanical and optical properties such as strength, brittleness, color, and opacity. The color of the original pulp is sometimes not so important as the ease with which it can be bleached, which may be considered a chemical property, and other chemical properties may be important in pulps designed for use in making cellulose esters.

There is no apparent relation between the physical properties and chemical composition of pulps. It is known that certain cooking conditions produce pulps with certain desirable mechanical properties and in general the well-cooked pulps rather than the under-cooked possess the better properties, but the corresponding differences in chemical composition are

<sup>44</sup> Rue, *Paper Trade J.*, 81, No. 16, 57 (1925).

unknown. The more complete cooking may, of course, leave a smaller residue of lignin in the pulp but it is not likely that the presence of more or less lignin within low limits has any direct bearing on strength. The weakness of certain over-cooked or burned pulps is probably due to slight and obscure chemical changes such as those that take place in drying or steaming wood at temperatures just above 100° C.

The color of pulps may be due to three causes: (1) The residual lignin; (2) coloring matter in the original wood not removed by the pulping process, and (3) coloring matter absorbed from the cooking liquor during the last part of the process. The chemistry of all these materials is obscure. The lignin is probably not the same as the lignin in the original wood which is not necessarily colored. In fact, certain pulps containing considerable lignin are only slightly colored. Woods containing tannin, such as chestnut, when cooked by the soda process develop a much darker color in the pulp than the original wood. In the pulping of aspen wood pictured in Fig. 13, it was noted that after the fourth hour the pulp was darker in color, evidently from adsorption of coloring matter from the liquor.

With such various and complex causes of color, it is not to be expected that the chemistry of bleaching is at all well known. Every wood, every process, and every set of cooking conditions might furnish a separate problem. It is known from practical experience that certain woods pulped in certain ways give easily-bleached pulps but the difference in chemical composition between easily-bleached and unbleachable pulps is not known. In general the pulps containing less lignin are easier to bleach since bleach is consumed in removing the lignin but this is not the only factor. The commercial bleaching process is by means of chlorine, usually applied in form of ordinary bleaching powder, and little attention has been given to other methods of bleaching. This is largely on account of the cheapness of the bleaching material and the ease with which it can be applied, but apparently chlorine is a very satisfactory bleach from other standpoints.

### Bleaching Wood Pulps

In one sense the bleaching of wood pulps is just another case of delignification by chlorination. Whether or not the lignin is the main cause of the color it certainly will be removed by the bleaching process, and since it is the main constituent of the pulp, aside from the cellulose, it is likely to require more chlorine for its removal than the other colored constituents, except, of course, where a large excess of chlorine is used in a vain attempt to remove some color. The lignin left in a wood pulp may not be of the same composition as that in the original wood, so that attempts to figure the theoretical amount of chlorine required for its removal

TABLE XLIV

## YIELDS OF PULP

(Results expressed in per cents, based on oven-dry weight of wood.)

Unbleached Pulps Sample No.	Nature of Cook No.	Yields Un- bleached Pulps			Yields Bleached Pulp			Yields Bleached Pulps		
		Bleaching Pulp	Powder	Yield	Bleaching Pulp	Powder	Yield	Bleaching Pulp	Powder	Yield
221 L	7	61.3	—	—	—	—	—	25	57.3	50
231 LR	7	39.4	30	39.2	—	—	—	—	—	—
221 W	8	47.3	25	47.9	6	45.6	12	38.8	8	38.7
231 WR	8	33.3	20	32.7	—	—	—	46.2	20	45.5
201 W	2	33.8	—	—	7	—	—	32.4	7	30
201 L	3	42.8	—	—	12	41.9	—	31.8	15	32.3
211 W	4	39.0	—	—	6	38.7	15	—	—	—
211 L	5	48.2	—	—	10	47.6	—	—	—	—
								25	46.2	—

are not very satisfactory. It has been shown,<sup>45</sup> however, that a sulfite pulp containing 11.92 per cent lignin after bleaching with bleaching powder equivalent to 8.74 per cent chlorine, contained 4.08 per cent lignin, a reduction of 7.84 per cent. If we take the figures of Heuser and Siebert<sup>46</sup> on chlorination of pine wood in which a total of 40.8 per cent chlorine was consumed, and assume 30 per cent lignin in the wood, 136 per cent chlorine on the weight of lignin is required for complete chlorination. In the example of bleaching just given 112 per cent chlorine was consumed which is as close as might be expected when the material was wood in one case and a crude pulp in the other. In this case where there was a large amount of lignin present and only a part was removed, most of the chlorine may have been used in removing the lignin but in most cases of bleaching a large excess of chlorine over the theoretical for removing the lignin is required for obtaining satisfactory color.

The other coloring matters besides lignin, therefore, seem to require a consumption of bleach out of proportion to their weight. This is shown in Table XLIV, where many of the bleachings do not change the weight of the pulp. Since, however, we do not know how much of these other materials may be present, except that the amount must be very small, further speculation on the subject is impossible.

The general effect of bleaching on the composition of various pulps has been shown in considerable detail by Mahood and Cable and since their work is referred to so much in this chapter their complete analytical results are given in Table XLV. In this table *L* indicates a light-cooked and *W* a well-cooked pulp. In the sulfite cooks *R* indicates a re-cook with a one per cent caustic soda liquor at 50 pounds steam pressure for one-half hour. The corresponding figures for four samples of cotton are given for comparison. Unfortunately an analysis of the wood used was not made but a standard analysis of the same species is given for comparison.

In commenting on the figures in this table only the total furfural values will be used, although these are divided into pentosan and methyl pentosan. There are several places in the table where the pentosan and methyl pentosan vary in different directions so that interesting conclusions might be drawn if we only knew more about the meaning of the methyl pentosan determination which, as we have shown, does not necessarily depend on the presence of methyl pentosan in the original wood. The methyl pentosan figures are included in the table, however, since they may be of more value some time when the analysis of the furfuroids is better understood.<sup>47</sup>

The effects of bleaching an under-cooked sulfite pulp are shown in lines 2-4. On account of the large amount of lignin present in this pulp,

<sup>45</sup> See lines 2 and 3 in Table XLV.

<sup>46</sup> See p. 234

<sup>47</sup> See Chapter IV, Part III.

TABLE

Sample Number or Designation	Bleaching Powder (35 Per Cent Avail- able Cl), Per Cent	Moisture	Ash	Cold-Water-Solu- ble 48 Hrs.	Hot-Water-Solu- ble 3 Hrs.	Alkali-Soluble <sup>1</sup> Per Cent NaOH in H <sub>2</sub> O	Acetic Acid by Hydrolysis	Ether Extract	Pentosan
<i>Spruce sulfite pulp, air-dried, results expressed in per cent</i>									
Spruce wood † ...	0.00	—	0.31	1.12	2.14	11.57	1.59	1.36	10.39
221 L ..... 0.00	7.99	1.72	2.54	2.76	9.77	0.24	2.10	5.43	
223 L ..... 25.00	6.44	1.36	1.53	3.98	18.14	0.03	0.63	7.07	
224 L ..... 50.00	6.19	1.21	2.15	3.57	16.21	0.02	0.66	6.67	
231 LR ..... 0.00	4.86	1.41	0.30	0.00	1.52	0.05	0.55	4.55	
232 LR ..... 3.00	4.80	1.57	0.68	0.58	2.97	0.08	0.97	3.95	
233 LR ..... 5.00	4.66	1.73	1.21	1.68	3.89	0.11	1.04	3.91	
234 LR ..... 8.00	5.32	1.78	0.83	1.13	4.62	0.08	0.77	4.17	
235 LR ..... 12.00	4.94	1.91	1.51	2.41	8.36	0.09	1.57	4.49	
221 W ..... 0.00	5.59	0.49	0.84	1.24	5.67	0.09	1.45	4.94	
223 W ..... 6.00	5.03	0.78	0.39	0.87	12.35	0.12	1.20	5.74	
224 W ..... 12.00	5.11	0.58	0.30	0.76	11.74	0.20	1.13	5.90	
225 W ..... 20.00	5.17	0.91	1.22	1.54	18.27	0.32	0.76	5.96	
231 WR ..... 0.00	4.41	0.75	0.29	0.12	0.14	0.02	0.73	2.61	
232 WR ..... 2.00	4.61	0.78	0.23	0.51	2.06	0.06	0.64	2.48	
233 WR ..... 5.00	5.18	1.01	0.00	0.28	4.17	0.00	0.72	2.51	
234 WR ..... 7.00	5.26	0.87	0.41	0.54	7.03	—	0.61	2.65	
235 WR ..... 12.00	5.34	1.00	0.93	1.76	16.38	—	0.53	3.35	
<i>Cotton, air-dried, results calculated on oven</i>									
Raw linters .. .	0.00	4.13	1.57	2.00	2.27	7.67	0.16	0.50	1.58
Absorbent cotton ..	0.00	4.34	0.11	0.00	0.00	1.75	0.04	0.31	0.58
Purified linters ‡ ..	2-3	2.67	0.52	0.33	0.23	1.52	0.10	0.24	1.11
Pulped linters ‡ ..	6-8	2.25	0.64	0.50	0.38	6.46	0.04	0.28	1.97
<i>Spruce soda and sulfate pulps, air-dried, results</i>									
201 L-Soda .. . 0.00	3.91	1.12	0.71	0.26	2.81	0.07	0.49	7.77	
202 L-Soda .. . 12.00	6.26	0.92	0.58	1.07	4.93	0.06	1.10	8.24	
203 L-Soda .. . 20.00	5.79	0.90	1.27	1.21	6.92	0.04	0.71	8.20	
201 W-Soda .. . 0.00	3.48	0.90	1.27	0.62	2.46	0.06	0.41	3.82	
203 W-Soda .. . 7.00	4.94	0.91	0.51	0.08	3.40	0.06	0.52	3.98	
205 W-Soda .. . 15.00	5.66	1.22	0.45	0.18	9.81	0.04	0.76	4.09	
211 L-Sulfate .. . 0.00	4.89	1.16	1.25	0.40	2.62	0.10	1.65	10.04	
212 L-Sulfate .. . 10.00	6.04	1.27	0.59	0.00	3.61	0.04	1.42	10.07	
213 L-Sulfate .. . 25.00	5.97	1.40	1.23	0.91	14.02	0.04	1.10	9.90	
211 W-Sulfate .. . 0.00	3.64	1.01	1.23	0.82	2.18	0.06	0.63	6.05	
213 W-Sulfate .. . 6.00	5.74	0.83	0.00	0.00	2.28	0.03	0.89	7.67	
214 W-Sulfate .. . 15.00	5.49	1.21	0.00	0.00	8.51	0.04	0.93	7.17	

\* The values given except those in the column headed "In Cellulose," are averages of two closely agreeing duplicates.

† Values obtained by Schorger, *J. Ind. Eng. Chem.*, 9, 556 (1917).

the removal of the lignin is the most noticeable change and this accounts for the apparent increase in cellulose and furfural which are little affected by the bleaching. The material soluble in one per cent alkali is increased

	Methylpentosan	Furfural	Alkali Soluble Per Cent NaOH 3 Hrs.	Methoxy Groups (CH <sub>3</sub> O)	In Cellulose								G. Cu per 100 G. of Sample
					Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl- pentosan	Furfural	Lignin (Non- cellulose)	
<i>cent, calculated on oven-dry (105° C) weight of pulp *</i>													
3.55	7.15	—	5.30	61.85	—	—	—	9.63	0.72	—	—	—	—
3.03	4.15	26.46	2.26	82.72	83.50 <sup>a</sup>	0.31	16.19	6.97	1.48	4.43	11.92	2.18	—
1.75	4.63	26.93	1.58	87.13	83.70	2.32	13.98	7.07	1.04	4.29	4.08	3.50	—
1.63	4.32	26.36	0.72	93.18	83.25	3.39	13.36	6.06	1.11	3.75	0.46	3.04	—
1.14	2.93	5.84	0.58	96.75	85.95	1.71	12.54	4.10	0.84	2.51	2.75	0.95	—
1.19	2.59	6.70	0.35	94.78	94.45	2.46	3.09	4.28	0.95	2.65	3.01	1.12	—
1.21	2.60	8.72	—	94.20	94.49	2.16	3.35	5.09	1.68	3.36	2.82	1.36	—
1.35	2.76	12.41	—	95.60	92.15	3.51	4.34	4.17	2.02	2.93	1.95	1.84	—
1.18	2.96	21.26	—	93.30	89.05	5.97	4.98	4.29	1.26	2.75	1.15	2.53	—
1.64	3.31	19.89	1.06	94.95	87.60	2.98	9.42	5.14	1.55	3.39	1.99	2.42	—
1.06	3.60	19.89	0.65	96.33	88.25	2.53	9.22	5.63	2.43	3.92	1.14	2.62	—
1.16	3.72	23.70	0.55	97.01	87.12	3.91	8.97	4.78	1.76	3.22	0.66	2.47	—
1.25	3.76	32.76	0.53	98.89	83.25	7.93	8.82	5.53	1.98	3.73	0.13	3.83	—
1.04	1.76	3.63	0.21	98.17	90.20	2.49	3.00	2.34	0.88	1.51	0.96	1.12	—
0.62	1.54	5.31	0.37	98.10	95.10	1.90	7.31	2.35	1.55	1.70	1.04	1.20	—
0.69	1.60	12.81	—	98.07	93.30	3.84	2.86	2.36	1.17	1.83	0.59	1.93	—
0.75	1.69	20.02	—	97.68	90.00	7.73	2.27	2.22	1.09	1.50	0.49	2.69	—
0.80	2.10	36.87	—	95.61	74.80	21.20	4.00	2.33	1.19	1.59	0.44	6.92	—
<i>dry (105° C) weight of material analyzed</i>													
0.52	0.98	12.22	0.36	89.75	83.19	1.87	14.95	0.46	0.32	0.20	8.15	4.55	—
0.48	0.30	6.20	0.39	98.93	87.60	12.20	0.12	0.50	0.85	0.16	0.36	1.13	—
0.46	0.63	3.72	0.37	99.32	97.40	2.60	0.00	0.45	0.77	0.30	1.35	0.87	—
0.70	1.27	16.67	0.31	97.90	88.30	11.70	0.00	1.31	1.03	0.88	0.12	2.57	—
<i>calculated on oven-dry (105° C) weight of pulp</i>													
1.14	4.82	5.93	0.89	93.17	85.66	7.81	6.53	7.31	1.52	4.59	4.03	1.59	—
1.18	5.09	12.03	0.57	94.26	60.57	34.19	5.24	7.45	1.33	4.63	5.86	1.76	—
1.35	5.12	17.06	0.32	94.77	53.01	35.07	11.92	6.80	1.50	4.32	4.55	2.40	—
1.25	2.54	5.89	0.47	96.20	80.30	13.27	6.43	3.42	1.54	2.33	2.11	1.09	—
1.66	2.76	7.14	0.26	97.16	55.93	34.22	9.85	3.87	1.88	2.71	2.66	1.66	—
0.63	2.54	22.15	0.29	97.05	51.50	37.80	10.70	3.41	1.92	2.48	2.22	3.61	—
0.92	6.09	8.61	0.68	94.56	84.20	6.31	9.49	9.96	1.29	6.10	3.39	1.38	—
0.64	6.05	11.64	0.26	94.00	64.70	23.98	11.32	8.30	1.70	5.26	5.53	1.67	—
0.85	6.00	31.04	0.25	94.56	56.87	31.55	11.58	8.46	1.46	5.27	4.04	3.93	—
1.07	3.79	5.51	—	96.17	81.80	10.31	8.07	5.81	1.62	3.85	1.88	1.46	—
1.35	4.51	7.10	0.24	95.68	72.20	18.72	9.08	6.95	1.01	4.28	3.43	1.58	—
1.62	4.22	20.47	0.18	95.40	62.95	26.90	10.15	6.20	0.97	3.84	2.64	2.98	—

\* The low moisture content of these two samples is due to their having been dried over a steam-heated radiator.

as is commonly the case when cellulose is chlorinated, although for some unaccountable reason the pulp bleached with 50 per cent bleach has a little less alkali-soluble than that bleached with 25 per cent. The amount soluble

in 7.14 per cent NaOH does not show similar results as might be expected but remains practically constant in the one unbleached and two bleached pulps. This is the only case where the two strengths of alkali do not give parallel results and it can be explained by the large amount of lignin in the crude pulp which is evidently much more soluble in the stronger alkali. The removal of the lignin by bleaching would, therefore, *decrease* this part of the alkali soluble matter at the same time *increasing* the alkali solubility of the cellulose and the two effects would tend to counterbalance. The methoxyl is decreased by bleaching although not in the same ratio as the lignin.

In the normal well-cooked sulfite pulp, the bleaching effects are not confused by the presence of a large amount of lignin. Here the alkali-soluble matter increases with the increased bleaching and the lignin and methoxyl decrease. The furfural increases slowly but this is probably not due to an increase in pentosans but rather to the formation of oxidized cellulose. It is interesting to note that the increase in "oxycellulose" as indicated by the increased furfural is not nearly so great as that indicated by increased solubility in alkali; also that the alpha-cellulose is not decreased as much as would be expected from the increase in alkali solubility of the pulp. These are points which must be given consideration in connection with some of the prevailing opinions in regard to the meaning of oxycellulose and alpha-cellulose determinations. The copper number determinations run parallel with the alkali solubility as would be expected. The figures on acetic acid by hydrolysis are very low and do not mean much except that the sulfite pulping process decreases this figure very much and possibly the bleaching of the well-cooked pulp increases it slowly. The water-soluble determinations probably do not show much except the degree of washing of the pulps. The ether-soluble determinations are also low and variable but they indicate that the sulfite process does not remove much ether-soluble material although the bleaching decreases it slightly. It is not known how much reliance can be placed on the moisture figures since it is not stated how much care was taken to bring the samples to equilibrium with air of the same humidity. If we assume that the moisture determinations were made on samples in equilibrium with the same moist air, some fairly definite deductions can be made. Although the results are not perfectly regular, there is an apparent decrease in the hygroscopicity of the sulfite pulps with bleaching.

The effect of bleaching on the pulps made by the alkalinizing processes will be considered next since the sulfite pulps re-cooked with caustic soda naturally show intermediate effects. The figures for lignin in the bleached soda and sulfate pulps are confusing since the lignin determination in every case shows an *increase* with the first bleaching and then a decrease with the second bleaching but never gets as low as in the unbleached pulp.

This increase cannot be in actual lignin but instead there must be something formed during bleaching of alkali pulps which is not soluble in 72 per cent sulfuric acid. It is apparently a part of both the lignin and cellulose as isolated by the analytical methods since the cellulose does not decrease when the "lignin" increases. Just what this something is and whether it occurs in other than spruce pulps are problems worthy of investigation since it may make a distinguishing characteristic for soda and sulfate pulps.

As would be expected, the crude alkali pulps are not so soluble in caustic soda as are the sulfite pulps. It would hardly be predicted, however, that bleaching would have less effect on the alkali solubility of the alkali pulps but this is evidently the case, especially with the more dilute alkali. The increase of furfural with bleaching is generally slight and irregular but in the case of the light-cooked sulfate pulp there is an apparent slight decrease.

Although the alkali solubility of the pulps is not increased greatly by bleaching, yet the amount of alpha-cellulose in the isolated cellulose is decreased very markedly. This fact furnishes still further confusion of our ideas in regard to the meaning of the alpha-cellulose determination. Although the unbleached alkaline pulps have a lower moisture content than the sulfite pulp under the same conditions, yet the bleaching causes a very definite increase in hygroscopicity so that the bleached alkaline pulps have a higher moisture content than the bleached sulfite pulps.

The sulfite pulps re-cooked with caustic soda show considerable losses during the re-cooking but the final yields are about the same as the straight soda cooks. The effects of bleaching these re-cooked pulps are intermediate between those of the straight sulfite and soda cooks. The "lignin" is apparently increased with slight bleaching and then is decreased on further bleaching, finally becoming lower than in the unbleached pulp. The alkali solubility is increased less than in the sulfite pulps with slight bleaching but to about the same extent on further bleaching. The alpha-cellulose is decreased more than in the sulfite and less than in the soda pulps. The furfural figures are irregular but indicate a slight decrease on bleaching. There is a slight tendency toward increased hygroscopicity on bleaching but not so great as in the case of the straight alkaline pulps.

#### Comparison of Wood Pulps with Cotton Cellulose

The main chemical differences between wood pulps and purified cotton cellulose lie in the pentose- and mannose-yielding residues left in the pulps even after severe cooking and bleaching treatments. Table XLV shows how little the pentose residues are affected by bleaching and Sherrard and Blanco have obtained 1.56 per cent mannose from a bleached sulfite pulp, from spruce wood. There are also lignin residues, or at least something

insoluble in 72 per cent sulfuric acid, which remains in the well purified pulps. In Table XLV there is only one sample, the well-cooked sulfite pulp bleached with 20 per cent bleaching powder, which is as low in "lignin" as the absorbent cotton or pulped linters. The sample of so-called purified linters (method of purification unknown), however, which in other respects is the nearest "pure cellulose" of all the samples shown in Table XLV, contains more "lignin" than several of the pulp samples. Evidently this material had been cooked with alkali and thus developed some of the unknown constituent previously mentioned which is determined as lignin. That it is not lignin in this case is shown by the cellulose determination which was 99.32 per cent.

The ether-soluble material is also slightly higher in the wood pulps, the only samples approaching the values for the purified cottons being the unbleached soda pulps. In methoxyl content, several of the wood pulps have lower values than the cottons. The fairly constant methoxyl in the cotton samples is very unexpected.

Few of the pulp samples show an alkali solubility as low as the purified linters but this is due largely to bleaching. One of the unbleached pulps is as low as the purified linters and four unbleached and one partly bleached are as low as the absorbent cotton in solubility in the 7.14 per cent alkali. The bleaching required to give a white or nearly white pulp greatly increases the alkali solubility but we have seen that this bleaching has little effect in the way of purifying the pulp, except in cases where considerable lignin was present, and, therefore, is not commonly required for any other purpose than for imparting a good color. The color has been shown to consist of very small amounts of material of unknown composition and, therefore, has little actual effect on the chemical composition of the pulp. In other words, wood pulp samples with an alkali solubility comparable with purified cotton can readily be obtained provided that a very small amount of coloring matter be permitted.

The exact requirements of the cellulose to be used in making cellulose esters are not known. There are specifications for the cotton cellulose used for this purpose but perhaps wood pulps might be satisfactory which did not comply with these specifications. Since a different set of impurities are to be guarded against in the case of wood pulps, a different set of tests should be prepared. It is known that sulfite pulps from spruce are being used in making viscose and it has been reported that wood pulps have been successfully used for nitration<sup>48</sup> but the detailed effects of variations in composition on the properties of the esters have never been published. If small pentose and mannose yielding residues are not harmful and if either a little color or a slightly higher alkali solubility can be allowed, then wood pulps can be readily prepared for use in making cellulose esters.

<sup>48</sup> Lenze, Pleus and Muller, *J. prakt. Chem.*, 7-9, 213 (1920-21).

## Chapter 5

### Decomposition by Concentrated Alkali

#### Methanol Formation

Intermediate in severity between the pulping of wood with caustic soda solutions and the fusion of wood with high concentrations of caustic alkalies, which forms the main subject for discussion in this chapter, lies some work by Ritter<sup>1</sup> on the formation of methanol from the methoxyl in wood in the presence of caustic soda solution at high temperatures. The conditions at the beginning of the treatment were very much the same as those used in pulping wood. The caustic soda was applied in a 7 per cent solution with about 21 per cent caustic on the weight of the wood and the pressure was 105 to 115 pounds. After three hours at pressure the water was allowed to distill off and the methanol was determined in the distillate. Then enough water was added to make the caustic solution 17½ per cent and the process repeated at a higher pressure. In the last two treatments, the maximum pressure was 200 pounds and in the last treatment no more methanol was obtained. Although this seems like a treatment with a maximum of 17½ per cent alkali, yet the autoclave in which the treatments were carried out was heated by a nitrate bath and had a very high heat capacity so that the temperature was still high after the water was distilled off. Therefore, during part of the time the temperature and concentration of alkali were both high.

Even during the first treatment more methanol was driven off than in the case of the soda pulping process, 2.12 per cent from oak and 1.47 per cent from Western yellow pine. Smaller amounts were given off on further treatments until finally 3.87 and 2.93 per cent were obtained from oak and pine, respectively. The residue of wood was then analyzed for methoxyl, the theoretical amount being found in the oak residue and none in the pine residue. This variation in results should be confirmed on other species since it may be a distinguishing characteristic between hard-woods and softwoods.

Although the methanol yields were different when expressed in terms of percentage of the wood used, yet exactly the same percentage of the original methoxyl content of the wood was recovered as methanol in both

<sup>1</sup> *Ind. Eng. Chem.*, 15, 1264 (1923).

cases, viz., 63 per cent. Ritter has called attention to the fact that this is the same percentage of original methoxyl as was found by Hawley and Aiyar<sup>2</sup> in the total volatile products obtained by destructive distillation of three different woods. There may be some important relationship here but it is not obvious.

Mahood and Cable<sup>3</sup> have also made some determinations of the methanol formed during a single fusion with caustic soda. They used three parts caustic soda to one part wood and gradually heated to 235° C., obtaining 2.33, 2.37 and 2.51 per cent methanol from elm (*Ulmus Americana*), oak (*Quercus alba*), and maple (*Acer saccharum*), respectively. The methanol yield from oak is lower than obtained by Ritter from the same species, showing that repeated less severe hydrolyses give more than one fusion at higher temperature and higher ratio of alkali. It was also found in this work that the methanol was given off in two distinct periods of the fusion. During the first period up to 160° C., about 25 per cent of the total was given off, then there was a period up to 180° C., when only about 5 per cent was obtained, the main fraction of 70 per cent coming off between 180° and 235° C.

### Fusion with Alkalies

The fusion of wood with caustic alkalies has been the foundation of the oxalic acid industry for many years and in this country has been only recently supplanted by the synthetic methods using carbon monoxide as the raw material.

Several investigators have worked on the fusion of wood with caustic alkalies but they have had different problems in view, have used different conditions, and determined the yield of different products. No one has worked on the details of the reaction under different conditions, with determinations of all the products, intermediate and final, and little effort has been made to correlate the results with the composition of the wood. There are gaps in the data which make it impossible to form a complete, satisfactory picture of the reaction and it will be necessary, therefore, to report in some detail the more important researches and then make what little correlation is possible.

### Thorn's Work on Oxalic Acid

Thorn<sup>4</sup> was the first to investigate in detail the fusion of wood with alkalies for the production of oxalic acid. He determined the effect of several variables on the yield of oxalic acid but did not study any of the

<sup>2</sup> *Ind. Eng. Chem.*, 14, 1056 (1922); see p. 207.

<sup>3</sup> *J. Ind. Eng. Chem.*, 11, 651 (1919).

<sup>4</sup> *Dingl. polytech. J.*, 210, 24 (1873).

other products. In varying the proportions of alkali and wood, it was found that the yield increased with increasing alkali up to a 4:1 ratio for caustic soda to wood and a 2:1 ratio for caustic potash. Higher ratios than these were not tried and all the other variables were studied at a 2:1 ratio\*. Most of the fusions were made at a temperature of 250° C., which was shown to be the optimum. Caustic potash gave a higher yield than caustic soda and high temperatures could be used with less danger of charring. It was found, however, that a mixture of 60 parts NaOH to 40 parts KOH gave almost as high yields as KOH alone. The reaction seemed to take a different course when 90 parts NaOH and 10 parts KOH were used for the fusion of 50 parts wood. At about 180° C., a strong exothermic reaction was started which would take the temperature to 360° C. without further heating, although with other mixtures of alkalies only a slight, easily controlled exothermic reaction took place.

A little work was done on different species with the conclusion that the softwoods gave higher yields than hardwoods. Of the five species used one hardwood, poplar, gave almost as high yields as pine and fir so that there are hardly enough data to make this a safe conclusion. Beech and oak, however, gave considerably less oxalic acid than the other three species.

It was noticed that when the fusion was made in thin layers, the yield of oxalic acid was generally higher than when the layers were thicker. This suggested oxidation as the cause of the higher yields and some experiments were made in which oxidation was encouraged by a current of hot air over the surface of the melt and by the addition of manganese dioxide. In neither case, however, was there any appreciable effect in the yields.

The maximum yield reported was 94.7 per cent oxalic acid (with 2 molecules water of crystallization) from two softwoods fused at 240°-250° C. with 2 parts alkali consisting of 40 parts KOH and 60 parts NaOH. Most of the other yields reported from fusions under similar conditions were about 80-82 per cent and no comment was made on the unusually high yields in these two cases.

### Acetic Acid from Fusion of Carbohydrates

Cross, Bevan and Isaac<sup>5</sup> later included some wood samples in a general study of the alkaline fusion of carbohydrates. They were especially interested in the production of acetic acid but they also determined oxalic acid in some cases. They used a 3:1 ratio of potassium hydroxide to carbohydrate material and found that temperatures of 200° to 250° C. gave the best results. At 150° C. for 48 hours, 18 per cent acetic acid was obtained from wood (species not given). At 200° to 250° C. (time not

\*J. Soc. Chem. Ind., 11, 966 (1892).

given) 28 per cent acetic acid was formed from pine wood in comparison with 29 to 37 per cent from other purer carbohydrate materials. At 250° C. for 8 hours, 79 per cent crystallized oxalic acid was formed from beech wood in comparison with 16 per cent from sugar.

It was concluded that the theoretical yield of acetic acid from the fusion of carbohydrates was 33½ per cent although the yield of 28 per cent from wood was considerably more than the theoretical on the basis of, say, 65 per cent carbohydrates in wood. The data are not given but the statement is made that the "results confirm for the production of acetic acid those of Thorn and others for oxalic acid, i.e., the yield of acid is increased as the proportion of alkali to carbohydrate increases from 1:3. The yield is greater, *ceteris paribus*, with potash than with soda and intermediate yields are obtained with mixtures of the alkalies."

Formic acid was not determined but the total volatile acids were computed as acetic acid. Although it was stated that the purity of the acetic acid was proven by the analysis of the silver salt, yet, in view of the later work of other investigators reported in the next few pages, it seems that considerable quantities of formic acid must have been present.

#### Fusion with Caustic Soda

Mahood and Cable<sup>6</sup> had in mind principally the production of acetic acid and, on account of the prevailing scarcity of caustic potash, used only caustic soda, so that their results might have commercial interest. The fusions were made in loosely covered iron crucibles. After a few attempts to use less alkali they decided on three parts alkali to one part wood and used this ratio throughout. The variables were time, temperature, and species.

The highest yields of total volatile acids and of formic acid were obtained at lower temperatures and longer periods of time. In two runs at 170° C. and 12 hours time, over 15 per cent formic acid was obtained from white oak and long-leaf pine. In the case of hard maple and elm, the maximum formic acid was obtained at 200° C. and 12 hours with yields of 12.2 and 13.5 per cent, respectively. At 230° C. there was still considerable formic acid formed during short periods of heating but after 1½ to 3 hours it began to disappear. At 260° C. there was very little formic acid present at any time.

The maximum yields of 21 per cent of acetic acid were obtained at 260° C. in 6 hours although yields almost as large were obtained at three hours with the same temperature and at 3-12 hours with 230° C. At higher temperatures than 260° C. it was difficult to prevent charring and ignition of the charge with consequent lower yields. The greatest differ-

<sup>6</sup> Loc. cit.

ence between the species was found in the yield of acetic acid, the softwood giving in all cases considerably lower yields than any of the hardwoods.

The conditions were varied with the purpose of obtaining the largest possible yields of acetic acid but the oxalic acid produced was also determined. The highest yields of oxalic acid ( $+ 2\text{H}_2\text{O}$ ), 70 to 74 per cent, were obtained at 200° C. with 6 and 12 hours fusion, a large increase taking place between the third and sixth hour. When heating at 230° C. higher yields were obtained than at 200° C. up to the third hour but on longer heating the acid was apparently decomposed. This decomposition by heat is shown very plainly by the fusion at 260° C. and 290° C. at which temperature less than 3 per cent oxalic acid was obtained. In general higher yields were obtained from the softwood than from the hardwoods.

The reactions of the formation of acetic and oxalic acids are apparently independent. They both progress together with increasing time or temperature until finally the amount of oxalic acid begins to decrease while the acetic continues to increase. The ratio of oxalic to acetic may, however, be as low as 1:1 at the beginning of the process and as high as 5:1 at the end, indicating that the two acids come from different sources. There is probably a relation between the formic and oxalic acids since there seems to be a tendency for the formic to decrease with time or temperature while the oxalic is increasing. It is very likely that formic acid is the primary and oxalic acid the secondary product of the decomposition of the wood.

Since cellulose and sugar produce oxalic acid on fusion with alkali, and since wood under the same conditions produces about as much oxalic acid as would be expected from its carbohydrate content, it has naturally been assumed that the carbohydrates in wood are the only source of oxalic acid. Both soda and sulfite pulp liquors have been shown to furnish oxalic acid on fusion with alkali but here again the yields were about what would be expected from the carbohydrate content.<sup>7</sup> In order to determine directly the possibility of lignin yielding oxalic acid on fusion with alkali, Hagglund<sup>8</sup> and Heuser<sup>9</sup> used lignin isolated by concentrated HCl and found no oxalic acid among the products. Before Hagglund's later publication, however, Heuser and Winsvold<sup>10</sup> reported that by better analytical methods they had found 20 per cent oxalic acid. In later publications<sup>11</sup> Heuser with Winsvold and Hermann has reported an exhaust-

<sup>7</sup> Heuser, Roesch and Gunkel, *Cellulosechemie*, II, 13 (1921).

<sup>8</sup> *Arkiv Kemi. Mineral. Geol.*, 7, 15 (1918), and *Inst für Ttskemi*, No 2 (1922). The latter article was also published in *Cellulosechemie*, IV, 73 (1923).

<sup>9</sup> *Cellulosechemie*, II, 113 (1921).

<sup>10</sup> *Cellulosechemie*, IV, 49 and 62 (1923), and V, 1 (1924).

tive series of experiments on the alkali fusion of lignin and wood and given a very good bibliography of the subject. Most of the remainder of this chapter will be taken directly from these articles.

Erdmann<sup>11</sup> was the first to discover the presence of aromatic substances in the products of the alkali fusion of wood. He worked with residues isolated from wood which are now known to have been mixtures of cellulose and lignin so that many of his conclusions were incorrect. His report of the formation of protocatechuic acid and pyrocatechol has, however, been frequently confirmed.

Lange<sup>12</sup> also made his experiments on indefinite fractions of wood but he was the first to designate as "lignic acids" the precipitate obtained on neutralizing with dilute sulfuric acid the filtered water solution of the melt. A large part of this precipitate was soluble in alcohol and a part of the alcohol solution could be reprecipitated by ether. The composition of these complex acidic substances has not been studied further and the term "lignic acids" is still used to designate a considerable portion of the products of the alkali fusion of lignin and wood.

Most of Heuser's experimental work has been done with lignin isolated from spruce wood by the Willstatter method. About ten times as much KOH as lignin was used and the fusions were usually made at 240°-290° C. When the fusions were made in a nickel crucible and in the presence of air, about 20 per cent oxalic acid (water free), 16 per cent protocatechuic acid, and 2 per cent pyrocatechol were formed. By excluding the air with hydrogen or nitrogen, the formation of oxalic acid was almost entirely prevented and at the same time the yields of protocatechuic acid and pyrocatechol were increased to 18 per cent and 5 per cent respectively. By using an iron crucible and excluding the air no oxalic acid was formed, the yield of pyrocatechol was increased to 21 per cent and the protocatechuic acid decreased to 10 per cent. The effect of an iron crucible in the presence of air was in the same direction of lowered yields of oxalic acid and protocatechuic acid and increased yield of pyrocatechol but not to the same extent as when air was excluded.

Apparently the protocatechuic acid is the precursor of both the oxalic acid and the pyrocatechol in this reaction because the fusion of pure protocatechuic acid gives both the other products, as much as 20 per cent oxalic acid in the presence of air and 26 per cent pyrocatechol when fused in iron in presence of hydrogen. The conversion of the first-formed protocatechuic acid into pyrocatechol during the fusion of the lignin can be greatly reduced by adding ammonium carbonate to the melt. The highest yield of protocatechuic acid, 23.5 per cent, was obtained with ammonium

<sup>11</sup> *Annalen der Chemie*, Ergänzungs Band V, 223 (1867).

<sup>12</sup> *Zeit. Physiol Ch.*, 14, 15 and 217 (1890) These publications are discussed in more detail in Chapter 3, Part II.

carbonate present. Carbon dioxide gas passed into the crucible did not have the same effect, however.

Usually about 30 per cent "lignic acids" were formed. Not much effect on the yield was observed when iron or nickel crucibles were used<sup>\*</sup> or with atmospheres of hydrogen or air. An atmosphere of carbon dioxide, however, increased the yield to 56 per cent and a low temperature fusion at 170°-210° C. gave 88 per cent lignic acids. Such a high yield is an indication that the lignic acids are the precursors of most of the other products obtained by the alkali fusion of lignin. There is no proof, however, that the lignic acids obtained in 88 per cent yield are the same as those which are obtained in most of the fusions to the extent of about 30 per cent. A sample of lignic acids after separation from the products of one fusion was subjected to another similar fusion and half of it was decomposed. Unfortunately, however, the products of decomposition were not determined.

In two fusions in nickel crucibles in the presence of air, the amount of CO<sub>2</sub> formed during the reaction was determined. Very little gas was given off during the fusion and the CO<sub>2</sub> was found in the form of K<sub>2</sub>CO<sub>3</sub> in the fused mass. About 28 per cent CO<sub>2</sub> was found, many times more than would be expected if it all came from the conversion of protocatechuic acid into pyrocatechol. Apparently most of the CO<sub>2</sub> is formed by oxidation and in fact fusion with alkali is commonly an oxidizing reaction.

Heuser did not report any attempt to find acetic or formic acids among the products from lignin but stated that they occurred in negligible quantities. Hägglund<sup>1a</sup> reported no acetic acid but identified formic acid without a quantitative determination.

Heuser made a few fusions of pure cellulose for comparison with his lignin fusions especially to determine whether any aromatic products were formed. He found no protocatechuic acid, no pyrocatechol, and not even enough of similar compounds to give a coloration with ferric chloride solution. He found also that, contrary to the experiments with lignin, no variation in yields was obtained by varying the metal of the crucible or the atmosphere surrounding the charge during fusion. The products obtained under varying conditions consisted of 90-91 per cent oxalic acid (water-free), 21-22 per cent acetic acid and 1.6-2.0 per cent formic acid. It is interesting to compare the composition of these products in terms of C, H and O with the raw material from which they were produced. Taking 90 parts of oxalic acid, 21 parts of acetic, and 2 parts of formic as the products from 100 parts of cellulose, the figures in the following table were computed.

\* *Cellulosechemie*, IV, 73 (1923).

## THE CHEMISTRY OF WOOD

TABLE XLVI  
COMPOSITION OF CELLULOSE AND ITS FUSION PRODUCTS  
(Computations from Heuser's results)

	Cellulose 100 Parts	Oxalic Acid 90 Parts	Acetic Acid 21 Parts	Formic Acid 2 Parts	Total Products 113 Parts
C .....	44.4	24	8.4	0.5	32.9
O .....	49.4	64	11.2	1.4	76.6
H .....	6.1	2	0.8	0.1	2.9

Only 32.9 parts C out of 44.4 parts in the original cellulose and 2.9 parts H out of 6.1 in the cellulose are found in the products, but 76.6 parts O are found in the products in comparison with only 49.4 parts in the cellulose. It is difficult to explain the origin of this excess oxygen since these yields were obtained even when the fusion was carried out in an atmosphere of hydrogen.

Finally Heuser made a series of experiments with spruce wood, the results of which are given in Table XLVII.

TABLE XLVII  
ALKALI FUSIONS OF SPRUCE WOOD  
(From Heuser)

Crucible	Atmosphere	Oxalic Acid Water-free Per Cent	Protocat- chic Acid Per Cent	Pyro- catechol Per Cent	Acetic Acid Per Cent	Formic Acid Per Cent
Nickel	Air	65.53	5.88	0.47	17.79	0.54
	"	65.60	6.10	0.64	18.03	2.32
Iron	Hydrogen	59.80	7.13	0.60	16.26	1.08
	"	59.33	2.00	6.98	15.36	1.17
		59.06	1.76	6.80	....	....

It may be dangerous to attempt to correlate these figures for wood with those previously given for cellulose and lignin, since the cellulose used was highly purified and does not correspond to the total carbohydrates in wood and since the lignin after separation from the wood may not give the same reactions as the original lignin in the wood. Even though such inaccuracies are understood to be possible, yet some interesting calculations can be made. If it is assumed that all the carbohydrates in the wood give the same yields of oxalic acid as were given by the purified cellulose used by Heuser, a wood with 67 per cent carbohydrates<sup>14</sup> would give 60.3 per cent oxalic acid from the cellulose alone. This corresponds very well to the yields shown in Table XLVII for the fusions made in an atmosphere of hydrogen so that no oxalic acid was formed from the lignin. When the fusions were made in air

<sup>14</sup>A probable figure for spruce wood. See p. 239.

an assumed lignin content of 28 per cent would be expected to furnish about 5.6 additional oxalic acid and bring the total up to 65.9 per cent. This theoretical yield corresponds very well to the 65.5 per cent oxalic acid figure in Table XLVII.

In the case of the acetic acid yields, the figures are not so close, the theoretical yield (22 per cent acetic acid from 67 per cent carbohydrates) being only 14.7 per cent compared with the actual yield of about 18 per cent. It is probable, therefore, either that the pentosans in the wood give a higher acetic acid yield than the hexosans or that the acetyl groups not found in isolated lignin furnish an additional amount of acetic acid.

In the same way the theoretical yields of pyrocatechol and protocatechuic acid can be computed. They do not approximate the actual yields quite so closely as in the case of the oxalic acid but the variations are all in the same directions as would be expected from the results with lignin alone.

As was stated at the beginning of the chapter, it is difficult to correlate the work of the different investigators on account of the wide variations in conditions. We are in position now, however, to account for the different results obtained. The high yields of oxalic acid reported by Heuser, 90 per cent water-free acid, are probably due to the high ratio of alkali to wood. He used a ratio of approximately 10, while the others used only 2 or 3.

The high acetic acid yields of Cross, Bevan and Isaac are probably due to the fact that their acetic acid contained considerable formic acid and they used low temperatures at which formic acid might remain undecomposed. Heuser obtained higher acetic acid yields than Mahood and Cable and this was probably due to the higher alkali ratio and to the use of potassium instead of sodium hydroxide.

One of the main points of interest in the alkaline fusion of wood from the standpoint of wood chemistry is the formation of aromatic products from the lignin, which gives at least an indication of its composition. This point is very completely discussed in Heuser's articles, and is referred to in Chapter 3, Part II.



# PART V

## WOOD AS AN INDUSTRIAL MATERIAL

### Chapter I

#### Physical Properties

There are several important physical properties of wood which are of direct interest in connection with chemical industrial uses of wood. The microscopic structure of wood must be discussed first in order to interpret the variations in these physical properties and it is also a subject on which some information is required in order to develop certain points of purely chemical nature. The absorption of liquids by wood is not only an important physical property but it bears closely on certain chemical subjects. All these properties will, therefore, be discussed briefly, although they are not strictly wood chemistry.

#### The Structure of Wood

Wood is homogeneous neither structurally nor chemically and a brief description of the structural features will, therefore, be given—just enough to give a general idea of the complexity of wood structure and its effect on the properties of wood. In microscopic detail the wood of different species of trees varies enough so that species, or at least groups of similar species, can be identified by skilled wood microscopists. These details are, however, out of place in this book and only the larger and more common structures will be discussed here.

Perhaps the best way to show the general structure is by means of a somewhat idealized enlarged drawing of a block of wood, such as Figs. 16 and 17. Micro-photographs may give a more complete and accurate record of experimental data but they have the disadvantage of requiring experience for proper interpretation. These figures are the result of diagrammatic interpretation by experts.<sup>1</sup> Fig. 16 represents a cube of white pine wood (*Pinus strobus*) about  $\frac{1}{16}$  inch on a side. The vertical direction in the block represents the vertical direction in the tree from

<sup>1</sup> Forest Products Laboratory, Technical Notes 209 and 210.

which the block was cut. Since most of the structural elements run in this direction, it is commonly called "longitudinal." The direction represented by the line A R is from the center of the tree toward the surface and is called the radial direction. The third direction, represented by the line T T, at right angles to the other two, is called "tangential."

The main part of the wood is seen to be made up of the walls of a series of longitudinal (vertical) cells. These are called the fibers or in

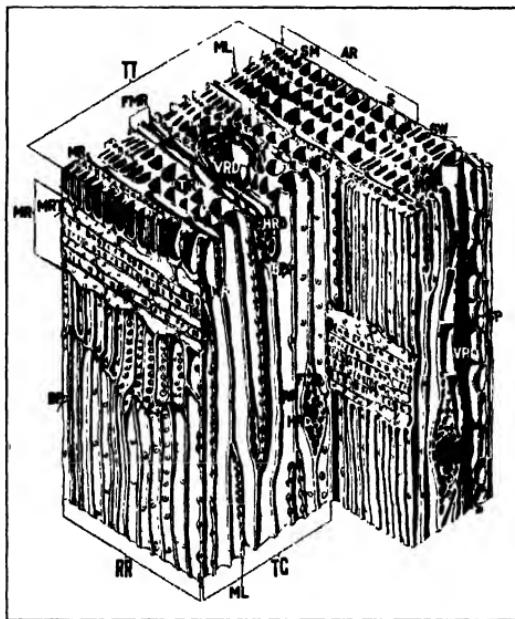


FIG. 16.—Sketch of Highly Magnified Block of White Pine Wood.

the strict sense, tracheids T R. The end of one series of tracheids and the beginning of another is shown on the left side surface R R. Contiguous tracheids possess a median wall layer in common, the middle lamella M L which appears as a cementing layer. The other tubular longitudinal spaces, larger than the cavities in the tracheids, are the vertical resin canals (sometimes called resin ducts) V R D. These are surrounded by specialized cells, shorter than the tracheids and capable of secreting resin.

The radial structures are called the wood rays M R, sometimes called

medullary rays. The cells making up the wood rays are much shorter than the tracheids and are called the ray cells. Some of these radial bands contain a horizontal resin canal H R D, which communicates directly with a vertical canal as shown near the lower right corner of the block. There are no main structural elements leading in a tangential direction but there are means of communication between the tracheids in the tangential direction, the bordered pits B P. There are also means of communication between the tracheids and the wood rays. These are in part small doubly bordered pits and in part window-like pits S P with a very narrow border and a wide pit membrane which is nothing but a local thinning out of the walls of the ray cells and of the tracheids.

It should be noted that some of the tracheids are larger in cross-section and have relatively thinner walls than others. These larger tracheids are formed in the earlier part of the season's growth and make up the spring wood S. The later growth of thicker walled tracheids forms the summer wood S M. The spring and summer woods together form an annual ring A R. These bands of growth can usually be seen with the naked eye on the cross-section of a piece of wood.

The other softwoods have a general structure very similar to white pine. Some have larger and some smaller resin canals, or they are wholly lacking. But aside from this, there are no major differences.

The hardwoods as a class have, however, some major distinguishing features. These are shown in Fig. 17 which represents a cube of hardwood of the same size as that in Fig. 16. Aside from the fibrous tissue F, which like the tracheids of the conifers, has a mechanical function, the hardwoods possess characteristic longitudinal structures, the vessels or ducts (pores, in cross-section) V. Vessels are composite structures which are made up of segments or cells arranged in vertical rows. The vessel segments are shorter and much larger in diameter than the fibers and their cavities are joined end to end through relatively large openings S C. The hardwood fibers are generally shorter and smaller in diameter than the softwood tracheids. The pits in the fibers of the hardwoods are much smaller and hence less conspicuous than those in the tracheids of the softwoods, but like the latter, they are bordered, except in extremely thick-walled fibers. The pits in the vessels connecting with the wood rays are semi-bordered or simple, but those connecting contiguous vessels are generally doubly bordered. Both kinds of pits are designated by P in the figure.

The hardwoods have larger, thinner walled, fibrous tissue in the spring-wood than in the summerwood, the same as the softwoods. In addition the hardwood springwood is sometimes further characterized by the presence of much larger pores than are found in the summerwood.

In some hardwoods, the ring porous woods, the larger pores are all in the springwood; in others, the diffuse porous woods, the pores are more nearly the same size and are fairly evenly distributed throughout the ring. The wood rays M R, though larger, the middle lamella M L, and the annual rings A R of the hardwoods are similar to those of the softwoods.

Figs. 16 and 17 apply to the structure of both heartwood and sapwood. Sapwood is the name applied to the wood of the outside part of the

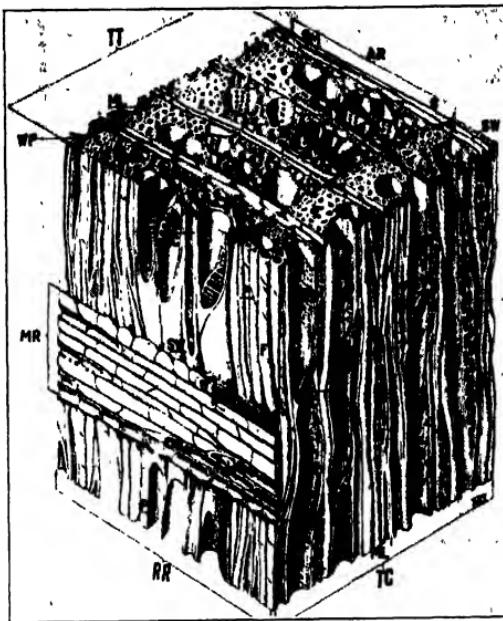


FIG. 17.—Sketch of Highly Magnified Block of Hardwood.

woody cylinder which still functions in the life processes of the tree. As new cells are added to the outer layer of sapwood during the growth of the tree some of the inner cells cease to function and become a part of the dead heartwood. Since the cells are fully grown and lignified while they are still in the sapwood there is no marked change in structure when they become heartwood. The marked difference in appearance between the heartwood and sapwood of certain species is due to variations in the amount of extraneous materials present. The thickness of the sapwood layer varies with different trees of the same species.

due to conditions of growth. The ratio of heart to sap may also vary at different periods in the growth of the same tree.

The variations in chemical composition of heartwood and sapwood, springwood and summerwood, are discussed in Part III, Chapter 6, and need not be further mentioned here, but there is a little information on the location of certain chemical constituents in the microscopic structure of wood which should be given here. The resin is normally found only in the resin canals, but in abnormally pitchy wood such as the "light-wood" of longleaf pine, it may be widely distributed in the rest of the wood. Another extraneous material, the storax in red gum wood,<sup>2</sup> is located in the special cells and canals in which it is secreted and transported. The water-soluble extractives, such as the tannins, are apparently well distributed throughout walls of the various wood elements as would be expected from the even distribution of the water. When unusually large amounts are present, however, the solid material may be found in the cell cavities. Starch and other reserve foodstuffs, more rarely certain extraneous compounds of unknown composition, are found in appreciable amount in the wood rays and in certain specialized cells which remain living in the sapwood and extend in rows with the grain of the wood—the *longitudinal wood parenchyma*. The only data we have on the location of cellulose or lignin in individual wood elements or the walls thereof are from Ritter's work on the distribution of lignin.<sup>3</sup> He found that the middle lamella was composed of lignin, probably entirely, and that considerable quantities of lignin were also distributed throughout the rest of the cell wall (the secondary layers).

Aside from this we have no evidence of the location of the major chemical constituents of wood. We do not know whether the lignin not in the middle lamella, the pentosans, or the readily hydrolyzable parts of the Cross and Bevan cellulose are concentrated more in one part of the secondary cell wall<sup>4</sup> than in another. We do not know whether the walls of the wood ray cells are the same in composition as those of the fibers or of the pores. They are all probably of the same general composition in that they are made up largely of cellulose and lignin, but how these may vary in properties or in composition we do not know. There is, however, one bit of evidence that the secondary cell wall<sup>5</sup> is made up of a homogeneous mixture of all of its constituents. Pure cellulose has an orderly arrangement of its molecules, or some other small aggregates, so that it transmits polarized light between crossed

<sup>2</sup> Mahood and Gerry, *Druggists' Circular*, Jan., 1921.

<sup>3</sup> *Ind. Eng. Chem.*, 17, 1194 (1925), cf Part II, Chapters 2 and 3.

<sup>4</sup> The botanists consider the middle lamella a part of the cell wall and frequently call it the primary cell wall. The term "secondary cell wall" therefore means that part of the total cell wall which is not middle lamella.

<sup>5</sup> See p. 18.

Nicols. Chemical wood pulps and the Cross and Bevan cellulose isolated from wood also transmit polarized light, so that whatever constituents they have making them different from pure cellulose are also probably arranged in the same manner as the aggregates of the pure cellulose. It is not at all difficult to conceive of this, since these other constituents are so similar to the pure cellulose chemically.<sup>6</sup> But the secondary cell wall, just as it occurs in wood, also transmits polarized light and it is carrying the same conception only a little further to assume that the lignin molecules or aggregates are also arranged in the same manner. Neither the lignin in the middle lamella nor lignin as isolated from wood by chemical methods transmits polarized light and if the aggregates of lignin in the secondary cell wall were of microscopic size they would appear as dark spots in the otherwise light cell wall when examined between crossed Nicols.

These conclusions might be confirmed or disproved by the study of another optical property. Considerable work has been done on the X-ray diffraction of pure cellulose but not enough combinations or mixtures, such as those mentioned above, have been studied to throw much light on the arrangement of wood constituents. Herzog<sup>7</sup> reports that cotton cellulose and wood pulp (composition unknown) have the same X-ray diagrams and appear identical but he did not study the more complicated forms of Cross and Bevan cellulose from wood or the wood fibers themselves. There is a chance for a lately developed technic to be of great service to the wood chemist.

### Strength of Wood

The strength of wood is entirely a mechanical subject and only such portions of it will be mentioned here as have some bearing on other parts of the monograph. The special literature of the subject may be found in various publications of the Forest Service and two recent books<sup>8</sup> give good general discussions. In many physical properties wood varies much more than it does in its chemical properties and the various strength factors are among these variable physical properties. In fact if the chemist were forced to draw his conclusions from such variable data as the timber testing engineer obtains, he would need to be more of a mathematician than he usually is in order to obtain the correct averages. The specific gravity, the rate of growth, the proportions of springwood and summerwood, cross grain, spiral grain, knots, checks, case hardening, the part of the tree from which the sample comes, are some of

the variables which affect the strength. In Fig. 19 it is shown how moisture content affects one strength factor and other strength factors may be affected more or less. It is not unreasonable, therefore, that the engineer is conservative in comparing strength values of different species,<sup>8</sup> that he refuses to base any conclusion on a small number of tests, and that he uses a high factor of safety in specifying timbers for construction work.

As might be expected from its structure, wood shows different mechanical properties in different directions. Its shearing strength is lower in the longitudinal direction but it has a higher crushing strength and tensile strength in this direction. Further, it splits more easily radially than tangentially except when the grain is interlocked.

The various strength factors are also affected by certain conditions which have very little apparent effect on the wood otherwise. The very beginning of decay which can be detected only by a microscopic examination may have considerable effect on the strength. Temperatures slightly below 100° C., such as may be used in kiln drying operations, if continued for a long time may have a noticeable effect on the strength of wood and temperatures of 110° to 120° C. may have a rapid and severe effect.

Wood is very slightly plastic at ordinary temperatures as is shown by the fact that a solid briquet can be made from sawdust by high pressure. In the vicinity of 100° C. and in the presence of steam some species become so plastic that they can be readily bent and retain the distorted shape after cooling.

### Penetrability

The ease with which liquids can be forced into wood is of interest chiefly in connection with preservative treatments or with chemical reactions like the pulping processes where it is desired to bring the reagent into contact with all parts of the chip. Most of the available data were obtained in experiments in treating wood with coal-tar creosote. There is very little correlation possible between penetrability and structure and there are several conflicting theories as to just how creosote or other liquids pass into and through wood under pressure. We will, therefore, state the generally accepted facts in regard to treatment with creosote and leave the details of experiments and theory to the special literature on the subject.<sup>9</sup>

The penetration of creosote into wood under pressure is very much greater in the longitudinal direction than in either of the other direc-

tions and there is commonly little difference between radial and tangential penetration. Sapwood is commonly easier to treat than heartwood. Summerwood is commonly easier to treat than springwood, especially in softwoods. Dry or partly dry woods are easier to treat than green woods. There is a wide variation in the ease of penetration of different species.

There is one satisfactory relation between structure and penetration. Red oaks, for instance, are very easily penetrated in the longitudinal direction through the pores, while white oaks with very similar structure are very difficult to penetrate. This difference is due to the fact that the pores of white oak are obstructed by peculiar, thin-walled, irregular, growths called tyloses (not shown in Fig. 17). In wood with pores not obstructed by tyloses the longitudinal penetration takes place through the pores but in hardwoods with obstructed pores, the path of the liquid is a subject of controversy. The debate hinges on whether or not the membranes of the bordered pits are perforated permitting liquids to pass from one tracheid to another.

Obviously, there is a great need for further information on the mechanism of the passage of liquids through wood. Much of this information may be obtained by purely structural, microscopic studies, but further information is also required on the transfusion of liquids absorbed in the cell wall which may be called a physical or physico-chemical study.

### Specific Heat

Only one set of determinations of the specific heat of wood has been made. Dunlap<sup>10</sup> found the average specific heat of several species between 0° and 106° C. to be 0.327. As might be expected from our information on the relatively slight variability of chemical composition of the cell walls of different species, he found little variation in specific heat and recommended the value 0.327 for all species. This is probably a safe average to use for all species except those which may contain unusually large amounts of extractive materials.

### Specific Gravity

In the same way it might be expected that the actual specific gravity of wood substance would vary only slightly in different species. Dunlap<sup>11</sup> found a variation from 1.50 to 1.57 in several species determined at 30° C. The determinations were made by floating the samples in a calcium nitrate solution of such a concentration that the small particles of wood neither rose nor sank and then determining the density of

<sup>10</sup> For. Serv. Bull. 110

<sup>11</sup> *J. Agr. Research*, II, 423 (1914).

TABLE XLVIII  
SPECIFIC GRAVITY AND SHRINKAGE OF SOME TYPICAL AMERICAN SPECIES

Common and Botanical Name 1	Locality where Grown 2	Volume when Green 3 4		Volume when Oven-Dry 5 6		Shrinkage from Green to Oven-dry Condition 7
		In Volume (Per Cent of Dimensions when Green)	Radial (Per Cent of Dimensions when Green)			
<i>Hardwoods</i>						
Alder, red ( <i>Alnus oregona</i> )	Washington	0.37	0.43	12.6	4.4	7.3
Ash, black ( <i>Fraxinus nigra</i> )	Michigan, Wisconsin	.46	.53	15.2	5.0	7.8
Ash, green ( <i>Fraxinus lanceolata</i> )	Missouri, Louisiana	.52	.61	12.5	4.6	7.1
Aspen ( <i>Populus tremuloides</i> )	Wisconsin	.36	.42	11.1	3.3	6.9
Basswood ( <i>Tilia americana</i> )	Pennsylvania, Wisconsin	.33	.40	15.8	6.6	9.3
Beech ( <i>Fagus atropunicea</i> )	Indiana, Pennsylvania	0.54	0.66	16.2	4.8	10.6
Birch, yellow ( <i>Betula lutea</i> )	Pennsylvania, Wisconsin	.54	.66	16.8	7.4	9.0
Chestnut ( <i>Castanea dentata</i> )	Maryland, Tennessee	.40	.46	11.6	3.4	6.7
Cottonwood ( <i>Populus deltoides</i> )	Missouri	.37	.43	14.1	3.9	9.2
Elm, white ( <i>Ulmus americana</i> )	Wisconsin, Pennsylvania	.44	.54	14.4	4.2	9.5
Gum, red ( <i>Liquidambar styraciflua</i> )	Missouri	.44	.53	15.0	5.2	9.9
Hickory, big shellbark ( <i>Hicoria laciniosa</i> )	Mississippi, Ohio	.62	...	19.2	7.6	12.6
Hickory, pignut ( <i>Hicoria glabra</i> )	Ohio, Mississippi, Pennsylvania, W. Virginia	.66	...	17.9	7.2	11.5
Maple, sugar ( <i>Acer saccharum</i> )	Indiana, Pennsylvania, Wisconsin	.56	.66	14.5	4.8	9.2
Oak, white ( <i>Quercus alba</i> )	Arkansas, Louisiana, Indiana	.60	.71	15.8	5.3	9.0

TABLE XLVIII—Continued

Common and Botanical Name	Locality where Grown	Specific Gravity, Oven-dry, Based on			Shrinkage from Green to Oven-dry Condition		
		Volume when Green	Volume when Oven-Dry	In Volume (Per Cent of Dimensions when Green)	Radial (Per Cent of Dimensions when Green)	Tangential (Per Cent of Dimensions when Green)	
1	2	3	4	5	6	7	
<i>Conifers</i>							
Cedar, Port Orford ( <i>Chamaecyparis lawsoniana</i> )	Oregon	.41	.47	10.7	5.2	8.1	
Cedar, western red ( <i>Thuja plicata</i> )	Washington, Montana	.31	.34	8.1	2.5	5.1	
Cypress, bald ( <i>Taxodium distichum</i> )	Louisiana, Missouri	.41	.47	10.7	3.8	6.0	
Douglas fir ( <i>Pseudotsuga taxifolia</i> )	Washington, Oregon	.45	.52	12.6	5.0	7.9	
Fir, balsam ( <i>Abies balsamea</i> )	Wisconsin	.34	.41	10.8	2.8	6.6	
Hemlock (eastern) ( <i>Tsuga canadensis</i> )	Tennessee, Wisconsin	.38	.44	10.4	3.0	6.4	
Pine, longleaf ( <i>Pinus palustris</i> )	Florida, Louisiana, Mississ.ippi	.55	.64	12.3	5.3	7.5	
Pine, western yellow ( <i>Pinus ponderosa</i> )	Colorado, Montana, Arizona, Washington, California	.38	.42	10.0	3.9	6.4	
Pine, white ( <i>Pinus strobus</i> )	Wisconsin	.36	.39	7.8	2.2	5.9	
Spruce, white ( <i>Picea canadensis</i> )	New Hampshire, Wisconsin	.36	.43	14.8	3.7	7.3	

the solution. This method actually gave the specific gravity of the wood containing the amount of absorbed water it would hold in equilibrium with a calcium nitrate solution of the concentration used and the specific gravity of dry wood substance was still undetermined. On account of the swelling of wood when it absorbs water, it is difficult even to decide whether these values are too high or too low. It may also be that the variations noted between different species were not due to varia-

tions in the specific gravity of the dry wood but rather to variations in the amount of water absorbed or in the amount of swelling.

It is interesting to note that one determination was made at 35° C. and the specific gravity found to be higher than that of the same wood at 30° C. Since more water is absorbed at lower temperatures (see last section of this chapter) this indicates that the water is absorbed with a decrease in gravity and that the values given above are lower than that of dry wood. On the other hand, some recent determinations<sup>12</sup> have been made of the specific gravity when in contact with benzene and carbon tetrachloride which are supposed to be very much less absorbed than water and in these cases the figures found were very close to 1.475. It cannot be assumed that there is no adsorption of these liquids, so this figure of 1.475 is still not the true specific gravity of wood substance although it is probably much nearer the true value than the 1.50 to 1.57 found by Dunlap. It is also probable that the higher specific gravity for a higher temperature reported by Dunlap was due to an experimental error.

The apparent specific gravity of wood (i.e., the specific gravity of wood in its entirety) varies widely as would be expected from its cellular structure. The proportion of air spaces to wood substance, a purely structural variation, accounts for most of the variations in the apparent specific gravity of wood but the presence of extraneous materials either in the cell cavities or absorbed in the cell walls may also increase the apparent specific gravity. Table XLVIII shows the variation in apparent specific gravity of a few important American species.<sup>13</sup> Much wider variations are found among tropical species.

### Conductivity

The few available data on the conductivity of heat by wood are given in Table XLIX, taken from the Smithsonian Physical Tables. The first six values are for "kiln dried" wood and no statement is made in regard to actual moisture content or to the direction in the wood in which the measurements were made. Probably, however, these conditions were the same with all species and if so the figures give a satisfactory comparison of several species with varying density. As would be expected from the cellular structure of wood, the heat conductivity decreases with increasing air spaces (with decreasing specific gravity). Somewhat the same relation between density and conductivity is shown in the next six values determined by another investigator. Here again neither the moisture content nor the direction in the wood are given and the high conductivity of greenheart in comparison with lignumvitæ may be due to differences

<sup>12</sup> Stamm, Unpublished report, For Prod. Lab.

<sup>13</sup> Newlin and Wilson, Dept. Agr. Bull. 556, 1917. The original table gives specific gravity, shrinkage, and various strength factors for 126 species.

in these variables or to a higher conductivity of the extraneous materials in the former species. The conductivity increases with temperature in all these species except greenheart. This again indicates that the high conductivity of this species is due to something besides wood substance.

The only figures we have on variation of conductivity in different directions are by Forbes<sup>14</sup> (reported in Landolt and Börnstein) and by

TABLE XLIX

## THERMAL CONDUCTIVITY OF WOOD

Grams-calories per sec. through thickness of 1 cm<sup>2</sup> per cm.<sup>2</sup> for 1° C. difference of temperature

Wood	Density of Total Wood	Conductivity at 20° C.	Conductivity at 100° C.
Cypress . . . . .	0.46	.00023	...
White Pine . . . . .	0.50	.00027	...
Mahogany . . . . .	0.55	.00031	...
Virginia Pine . . . . .	0.55	.00033	...
Oak . . . . .	0.61	.00035	...
Hard Maple . . . . .	0.71	.00038	...
Basswood . . . . .	0.90	.00036	.00041
Greenheart . . . . .	1.08	.00112	.00110
Lignumvitæ . . . . .	1.16	.00060	.00072
Mahogany . . . . .	0.55	.00051	.00060
Oak . . . . .	0.65	.00058	.00061
Whitewood . . . . .	0.58	.00041	.00045

Barratt<sup>15</sup> (reported in Kochler's "Properties and Uses of Wood"). The former gives values of 0.000088 and 0.00030 for pine wood in the radial and longitudinal directions, respectively. The latter gives 0.00016 and .00044 for red gum wood "across the fiber" and "along the fiber" respectively without stating whether the former direction was radial or tangential.

It is very evident that more experimental work is needed on this subject and that the moisture content of the wood and the direction of the measurement through the wood should be known in order to make the results satisfactory.

Much the same unsatisfactory condition exists in the data on the electrical conductivity.<sup>16</sup> Apparently perfectly dry wood is a very poor conductor of electricity so that even a small amount of absorbed water increases the conductivity very much. All of the available figures are valueless since they were obtained on wood with unknown moisture contents and the very wide variations are probably due to different moisture contents. It appears probable from these figures, however, that the

<sup>14</sup> Proc. Roy. Soc. Edinburgh, 8, 62 (1872-75).

<sup>15</sup> Proc. Phys. Soc. London, 27, 81 (1914)

<sup>16</sup> Muller, Electrotech. Z., 13, 72 (1842). Pierce, Proc. Am. Acad. Arts Sci., 30, 390 (1894). Curtis, Bur. Standards Bull. 11, 359 (1915).

electrical like the heat conductivity is much greater in the longitudinal direction than in the other directions.

TABLE L  
COEFFICIENT OF EXPANSION OF WOOD  
Change in length per unit length per degree C.

	Longitudinal	Radial	Tangential
Red Oak .....	$3.6 \times 10^{-6}$	$29.3 \times 10^{-6}$	$41.9 \times 10^{-6}$
Yellow Birch .....	$2.5 \times 10^{-6}$	$27.2 \times 10^{-6}$	$30.0 \times 10^{-6}$
Yellow Poplar .....	$1.7 \times 10^{-6}$	$24.2 \times 10^{-6}$	$26.7 \times 10^{-6}$
White Pine .....	$3.8 \times 10^{-6}$	....	....
Yellow Pine .....	$3.8 \times 10^{-6}$	....	....
Black Walnut .....	$3.2 \times 10^{-6}$	....	....

### Thermal Expansion

The first work on the expansion of wood by heat<sup>17</sup> was done with a special apparatus designed for use with metals and the investigator had no means for controlling the moisture content of the wood during the experiments. He realized the importance of this point and admitted that the results were not accurate. The expansion also was measured in only two directions, parallel to the fiber and across the fiber, without determining whether the latter direction was tangential or radial. This work, however, indicated strongly that the expansion across the fiber was much greater than parallel to the fiber.

The later work<sup>18</sup> which was carried out under carefully controlled moisture conditions is recorded in Table L. These results show a considerable variation between species but the general conclusion can be drawn that the expansion is much less in the longitudinal than in either of the other directions and slightly less in the radial than in the tangential direction. The same general relation holds here that is found in the case of swelling with the absorption of water.

### Absorption of Water

This is also a subject on which we have little experimental data although the absorption of water by wood has an immense practical bearing in connection with the drying, shrinking and swelling of wood as well as on its strength. We have only three bits of fundamental data on which to base any conception of the wood-water relationship: (1) the total heat of absorption of water by wood in presence of excess water is known; (2) the moisture content of wood in equilibrium with air at different humidities and at two different temperatures has been determined;

<sup>17</sup> Glatzel, *Pogg. Ann.*, 160, 497 (1877).

<sup>18</sup> Unpublished report by C. A. Menzel, Forest Products Laboratory (1921).

(3) it has been found that the strength of wood decreases with increase of moisture content until a certain maximum moisture content is reached but beyond this point moisture has no effect on strength. There are a large number of miscellaneous observations which are of assistance in working out the general theory but much of the evidence required for a satisfactory development of the picture is lacking.

One difficulty encountered at the start is the complex structure of wood which gives it different properties in different directions. Another difficulty is that much of the experimental work has been done on blocks of some size so that the condition of equilibrium at the surface has been confused by the effects of transpiration within the block. We believe that the best way to develop the subject is first to discuss from a purely theoretical standpoint the equilibrium between wood substance and water and then try to correlate the conclusions with the structure of wood and with some of the facts in regard to the absorption of moisture by wood.

Wood has a positive heat of absorption for water. Only the total heat with excess water has been determined and the amount of heat given off during the absorption of various small amounts of water is not known. Dunlap<sup>19</sup> found the total heat of absorption at 0° C. to be 16.6 to 19.6 calories per gram of wood of three different species. Not enough determinations were made to conclude whether there is any regular variation between different species or to determine what effect different conditions of drying might have.

A positive heat of absorption would be expected from the previously known fact that wood contains moisture when in equilibrium with air even at low humidities. The only quantitative expression of this fact that we have is given in Fig. 18<sup>20</sup>. The data for the two temperatures were obtained by different investigations with different methods and, therefore, are not strictly comparable. Curve A, although it is stated to give values at 24° C., is really the result of determinations made at room temperature with variations of 5-6° C. on either side of 24° C. Curve B is an average of results on five species at four or five humidities for each species but the data are not very satisfactory on account of the wide variations from the average. The two curves are, however, sufficiently comparable and accurate for the purpose of this qualitative discussion. Curve A indicates that a maximum absorption is reached at ordinary temperatures when the moisture content of the wood comes to about 33 per cent. The data on the effect of moisture on the strength

<sup>19</sup> Unpublished report, Forest Products Laboratory, 1912.

<sup>20</sup> Curve A is an average curve for seven species of wood as determined by M. E. Dunlap, Forest Products Laboratory, 1919. Curve B is taken from an unpublished report by McKenzie, Forest Products Laboratory, 1912.

of wood also show a similar saturation point at 21 to 34 per cent moisture. Fig. 19 gives some typical data of this kind.<sup>21</sup> Here we have curves which intersect straight lines at points which indicate the limit for the absorp-

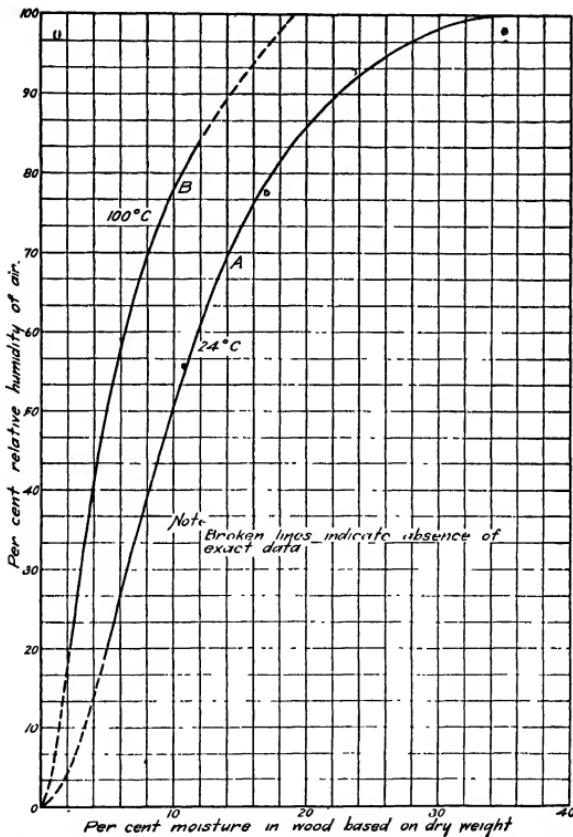


FIG. 18.—Moisture Contents of Wood in Equilibrium with Atmosphere of Varying Humidity and Temperature.

tion of water by wood at least in so far as the absorption affects the strength of the wood.

On account of the fact that there is a positive heat of absorption of water by wood, we would expect the amount of absorption to be greater

<sup>21</sup> Tiemann, For. Serv. Circ., 108 (1907).

at lower temperatures. This is also indicated in Fig. 18 since the low temperature curve A always shows higher moisture content than the high temperature curve B, other conditions than temperature being the

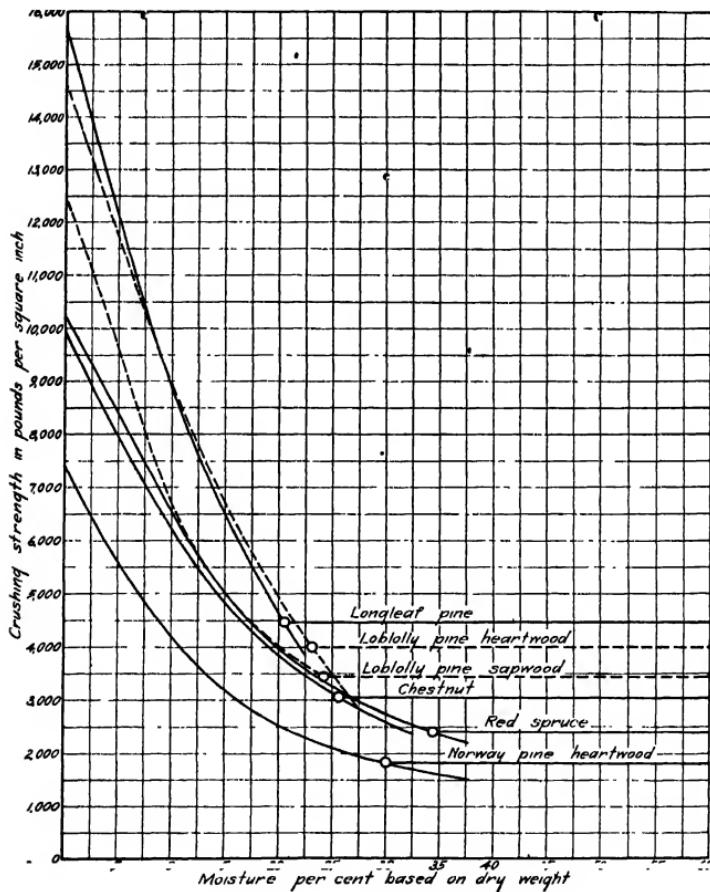


FIG. 19.—Relation between Strength and Moisture Content of Wood.

same. We have no confirmation of this point from strength data since the effect of moisture on strength has not been determined at different temperatures.

From these few data, therefore, it seems that water is absorbed by wood with lowering of vapor pressure and giving off of heat up to a limit or saturation point. As is the case with other absorptions of volatile liquids by solids, the exact mechanism is not known. It may be condensation in small capillaries, or surface adsorption on a peculiar fine structure existing in wood, or the water may form a solid solution with the wood entering into the crystalline structure of the cell wall or perhaps there may not be any essential difference between these mechanisms. At least for the purpose of further discussion, it does not make much difference which type of absorption is assumed.

The absorption of water by wood is probably not completely reversible although it may be reversible over most of its range. There are evidences that a wood once completely dried or subjected to high temperatures without complete drying may not absorb water so rapidly nor reach so high a moisture content at the same humidity as before. There are no quantitative figures on this subject nor even any data to show the relative effects of complete drying and high temperatures.

We are now forced to complicate this fairly simple and satisfactory picture of the absorption of water by wood substance by bringing in the subject of wood structure. The upper ends of the curves in Fig. 18 are not quite so accurate as they seem to be. There is an apparent equilibrium but not a true one where these lines seem to show an equilibrium moisture content of wood in contact with air of 100 per cent humidity. The determinations of relative humidity from which these curves were drawn were not accurate enough to show the exact course of the curves near this point but there are other data to indicate that they do not actually reach the vapor pressure of pure water until the moisture content of the wood is far beyond 32 per cent. McKenzie<sup>22</sup> found that blocks of spruce wood 1 inch x 1 inch x 6 inches held at 12° C. in air saturated with water vapor, took up 43.2 per cent water in 79 days and the absorption was still taking place although slowly. The rate of absorption in blocks of this size is affected by the transfusion of the moisture from the surface to the interior so that the absorption curve cannot be readily interpreted. It will not be given here but is enough to note that the absorption had gone far beyond the saturation point for wood substance as previously determined. If our previous conclusions in regard to the saturation point of wood substance are correct, this additional absorption must be due to the wood structure.

We have seen that wood is made up largely of small cells. The open spaces inside these cells may be as small as 0.01 mm in diameter throughout most of their length and perhaps much smaller near the ends. They are, therefore, small enough to act as capillary spaces and hold water

\* Unpublished report, Forest Products Laboratory.

at a reduced vapor pressure. In a water saturated atmosphere, therefore, these capillaries may condense water and the structure of wood may accordingly account for the absorption beyond the saturation point of the wood substance. A capillary even as small as 0.001 mm in diameter will, however, reduce the vapor pressure of water contained in it by only 0.1 per cent that of pure water, or 0.1 per cent reduction in relative humidity and this is a unit too small to plot on the scale of Fig. 18. This explains the *apparent* equilibrium between wood and water-saturated air when the moisture content of the wood has reached about 30 per cent. The absorption of water by the wood substance, which has a comparatively large effect on the vapor pressure of the absorbed water over most of its range, is nearly finished and the condensation of water in the microscopic capillaries of the wood structure, which has but a slight effect on the vapor pressure, is just beginning at the time this apparent equilibrium is reached. If we could obtain the wood in homogeneous form without the cell structure, it would probably reach an equilibrium with water-saturated air similar to that shown in Fig. 18. Schorger's gelatinized wood<sup>23</sup> offers the possibility of such an experiment. This gelatinized wood, in which the fibrous structure had been destroyed, was found to be slightly more hygroscopic than ordinary wood in contact with low-humidity air. This confirms the previous conclusions that the fibrous structure of wood has no effect on the equilibrium between wood and air at low humidity.

The swelling and shrinking of wood substance as it absorbs or gives off water was not discussed from the theoretical standpoint without reference to wood structure, as was done in the case of the heat effect and the moisture equilibrium, because we really have no data on this subject. It is difficult to obtain data on swelling which may not be affected by the structure or, in the swelling of a block of wood as it absorbs moisture, to divorce the effects due to microscopic structure from those due to sub-microscopic structure. It need only be noted in this connection that the swelling and shrinking of wood take place only below the saturation limit of wood for water in conformation with the effect of moisture on strength and the apparent equilibrium between wood and water-saturated air. In other words, water held in the microscopic cell cavities does not cause any swelling of the wood.

The data on the shrinkage of wood shows that there is a great difference in the amount of shrinkage which takes place simultaneously in the three directions. The shrinkage of different species when drying from the green wood to dry condition varies from 5.1 to 12.6 per cent in the tangential direction and from 2.2 to 7.6 per cent in the radial

<sup>23</sup> *Ind. Eng. Chem.*, 15, 812 (1923).

direction.<sup>24</sup> The longitudinal shrinkage was not determined in this set of experiments but it is very much smaller than either the tangential or radial shrinkages, usually being about 0.1 to 0.3 per cent in total shrinkage from the green to dry condition. It is evident from these figures that the effects of shrinking cannot be due to the structure of the wood. That is, if wood substance shrinks equally in all directions, it is impossible to account for such variations as are found for the shrinkage in the three directions in wood. If, however, it is assumed that each fibrous cell in wood shrinks more in cross section than in length, then the structure, in conjunction with this assumption, explains the known variations. Most of the cells of wood (the fibers and vessels) are arranged with their long axes in the longitudinal direction. If, therefore, these cells shrink mostly in cross section, the resulting shrinkage in a block of wood will be mostly in the radial and tangential directions. There are, however, other cellular aggregates of smaller size, the wood rays, in which the cells are arranged with their long axes in the radial direction. If these cells also shrink only slightly in the direction of their long axes, they will tend to prevent the shrinkage of the wood in this, the radial, direction. The structure of the wood, therefore, correlates very well with the assumption of directional shrinkage in the cell walls in explaining the greater shrinkage in the tangential than in the radial direction and the relatively very small shrinkage in the longitudinal direction.

This assumption of directional shrinkage is not without value in other fields. We have seen that the molecules or other small aggregates of cellulose in the cell wall are arranged in an orderly pattern and that possibly some of the other cell wall constituents are arranged in the same pattern. It has already been suggested on p. 289 that the water absorbed by wood enters into this arrangement of molecules or other aggregates and if it enters in such a way as to spread them apart in a direction radial or tangential to the long axis of the fiber, the directional swelling we have been assuming would be the result. Here is another subject on which X-ray diffraction research might be of great value to the wood technologist and here also is a suggestion to the worker in that field that the moisture content of his material may have an important influence on his results.

The increase in cross-sectional area with the amount of moisture absorbed is practically a straight line relation between zero moisture content and the saturation point.<sup>25</sup> This is not what would be expected when we consider that the reduction in the vapor pressure of the absorbed

\* See Table XLIX. There are certain species which show more or less shrinkage than these.

<sup>25</sup> Goss, Forest Service Bull. 122, 1913.

water follows a curve that is distinctly S-shaped. Apparently, therefore, there is no direct relation between the reduction in vapor pressure and the amount of swelling due to the absorbed water. It would be of interest to be able to obtain a graphic representation of the relation between amount of water absorbed and the heat of absorption.

The evidence is incomplete in regard to the reversability of the shrinking and swelling with moisture changes. In Forest Service Bulletin 122, it is reported that re-absorption of 8 per cent water after drying at 100° C. caused a swelling only very slightly less than that found for 8 per cent water before drying. On the other hand, steaming wood at 28 pounds pressure for 20 hours was found<sup>20</sup> to decrease the swelling to only about one-half that of unsteamed wood when the two were compared between the same (but unknown) two conditions of atmospheric humidity. Less moisture was present in the steamed wood after coming to equilibrium and the difference in swelling was due partly to difference in amount of moisture absorbed and partly to variation in the relation between moisture content and swelling. A chemical change due to hydrolysis might also account for these changes in swelling and moisture absorption.

In the previous discussion, we have developed the subjects of the vapor pressure, swelling, and heat effects when water is absorbed by wood and it might be thought that these subjects were all that were required for a discussion of the drying of wood. But here again the structure of the wood is the controlling factor in the process. Under the same conditions of temperature and humidity of the surrounding air, wood dries more rapidly from a transverse surface than from a tangential surface and more rapidly from a tangential than from a radial surface. This is not due to any differences in the vapor pressure of the water on these surfaces but to the fact that the water on the very surface is quickly removed and the rate of drying is then affected mostly by the rate at which the water transfuses through wood; in other words, water transfuses through wood more rapidly in the longitudinal direction than in the radial and more rapidly in the radial than in the tangential. This corresponds again to the proportions of long cell axes in these three directions but we have no direct evidence that the transfusion of water in the cell wall is any more rapid in one direction than in another. The passage of water in vapor form through the cell cavities might also be the explanation for the more rapid movement of the water in the longitudinal and radial directions. As a matter of fact we have not enough data on which to base any clear conception on the detailed mechanism of the movement of water through wood from a region of high moisture content to one of low moisture content. The only aid to such a conception that we can procure from the purely theoretical standpoint

<sup>20</sup> N. deW. Betts, unpublished report, Forest Products Laboratory, 1914.

is that the movement of water in wood from a high to a low moisture content will be appreciable only within the range of moisture content below the saturation point. Above this point the difference in the vapor pressure of the water between regions of different moisture content has been shown to be very small, and differences in vapor pressure are at least measures of the difference in potential which causes transfusion as liquid within the cell wall even if they are not the actual driving force as would be the case in evaporation into the cell cavities and movement in the form of vapor.

There are many interesting and important problems in connection with the commercial drying of wood which we will not consider here since they do not lie within the province of this book. For a discussion of these problems the reader is referred to the special literature of the subject.<sup>27</sup> After the previous discussions of the complexity of wood structure and the variations in different directions of such important properties as shrinking and moisture transfusion, it can readily be seen that the commercial drying of wood is no simple problem.

We do not have enough data to determine whether there is a considerable and consistent variation between species in the amount of water absorbed by them. The curves of the different species which make up the average curve B in Fig. 16 do not vary greatly one from another except near the upper end where, as we have seen, it is difficult to locate accurately the 100 per cent humidity point. Even here the greatest variation in seven species is between 30 and 37 per cent for the saturation point. On the other hand, the curves in Fig. 17 show variations between 21 and 34 per cent water at the saturation point as determined by the effect of moisture on strength. Only one species, longleaf pine, was used in both sets of experiments and it showed a saturation point of 36 per cent by the absorption method and 21 per cent by the strength method. It is possible that variations between different samples of wood from the same species may account for this difference or more likely the previous conditions of treatment or storage may be the explanation. With such meagre and conflicting data, it is idle to speculate further.

Apparently water is much more strongly absorbed by wood than are other volatile liquids but we have very little experimental data on the subject. In an unpublished University of Wisconsin thesis<sup>28</sup> a comparison was made of the rate of absorption of volatile liquids by sawdust from air saturated with the vapors of water, xylene, and kerosene. The rate of absorption was much more rapid in the case of water and

the apparent maximum was about 30 per cent instead of about 5 per cent for the xylene and kerosene. It was also shown that water would largely replace xylene from xylene-saturated wood when the air was saturated with vapors of both liquids. Dunlap<sup>29</sup> also determined the total heat of absorption of coal tar creosote and turpentine by wood to be, respectively 5.0 and 2.3 calories per gram of wood. There is need for much more data on the absorption by wood of volatile liquids other than water and on the correlated subjects of swelling and transmutation.

*\* Loc. cit.*

## Chapter .2

### The Deterioration of Wood

The deterioration of wood under various conditions of use is a very important subject from the standpoint of changes in chemical composition as well as the weakening and failure of structural timbers. Only the changes in chemical composition and natural resistance to various forms of deterioration will be discussed here since only these subjects are directly connected with wood chemistry. The artificial treatment of wood to prevent deterioration is not closely related except that it may be considered an imitation of the natural method of producing durable woods.

#### The Decay of Wood

The decay of wood is not a purely chemical process such as the corrosion of metals or the weathering of stone, it is not simply oxidation or hydration, but is a profound decomposition due to the action of certain low forms of plant life, the fungi. When wood is exposed to air, light and moisture there is probably a slight weathering action as shown by the change of color of the surface, but this is of little consequence and there is no information on the chemical action which takes place. The disintegration of wood due to "weathering" as distinguished from fungus attack is apparently a physical effect caused by rapid changes in moisture content and the consequent stresses from rapid swelling and shrinking. When the conditions under which it is kept are such that fungi cannot exist, as for instance too little or too much moisture, or the presence of toxic chemicals, wood will last almost indefinitely. Unpainted but perfectly sound original timbers can be found in buildings centuries old, sound logs of other geological ages have been removed from glacial clays, and trunks of certain naturally durable species have been found almost intact hundreds of years after they have fallen, the minimum elapsed time being determined by the age of another tree growing on top of the fallen trunk.

A detailed description of the wood-destroying fungi will not be undertaken since that is a biological or pathological rather than a chemical subject. It is sufficient to state that there are a large number of species recognized by the pathologist and that to a certain extent each one

specializes on a certain wood or group of woods and has its own particular conditions under which it best thrives. They propagate by means of spores and are sufficiently prevalent that any susceptible piece of wood is sure to be attacked.

The mechanism of the fungus attack is not known in detail but it is probable that the primary chemical action on the wood is due to an enzyme. In fact, several enzymes from wood-destroying fungi have been isolated and some have been named but further than that the details are lacking.<sup>1</sup> It is also unknown just what chemical compounds are elaborated from the wood by the enzyme or fungus before assimilation.

The effect of decay on the physical properties of wood has, of course, been noted for a long time since this is such an important subject in connection with the use of wood under conditions where decay can take place. The wood may be discolored and weakened at the very beginning of the attack, and even before a very large amount of wood has been destroyed, as shown by loss in weight, it may be greatly modified in physical properties. Finally a considerable loss in weight occurs and only a powdery or fibrous residue is left which bears no resemblance to the original wood. Different species of fungi have different visible effects on wood, and two general classes, the brown rots, and the white rots, are named from the color of decayed wood.

The chemical changes which accompany these well-known physical changes have been studied only recently and not in great detail. The first statements in regard to chemical changes during decay were made by the plant pathologists as a result of studying the partly decayed wood under the microscope. They found that one of the first effects was that the wood "took the cellulose stain" which it did not do when sound and therefore concluded that the wood had been "delignified." It was not known at that time that the same kind of an effect could be obtained by mechanical means<sup>2</sup> and the danger of drawing such a conclusion was not recognized.

The first chemical analysis of decayed wood was made by Rose and Lisse in 1917.<sup>3</sup> They worked on samples of sound, partly decayed, and completely decayed Douglas fir wood with the results shown in Table I.I. According to this table the most striking effects are the increase in alkali-soluble constituents and the decrease in cellulose. There is also

<sup>1</sup> See references in "The Diagnosis of Decay in Wood," by E. E. Hubert, *Jour. Agr. Res.*, XXIX, 523 (1924). This article also contains a very good description of the action of fungi on wood from the pathological standpoint.

<sup>2</sup> Robinson, *Phil Trans Roy Soc. Lond.*, Series B, 210, 54 (1920). Robinson found, on examining the locality where compression failure had taken place, that where the fibers were ruptured they were stained blue (the cellulose color) by the ZnCl—I stain. Normal wood is stained yellowish green (the lignin color) by this reagent.

<sup>3</sup> *J. Ind. Eng. Chem.*, 9, 284 (1917).

TABLE LI  
ANALYSES OF SOUND AND DECAYED DOUGLAS FIR WOOD

Determination	Sound Per Cent	Partial Rot Per Cent	Complete Rot Per Cent
Cold-water-soluble .....	4.03	1.75*	1.16
Hot-water-soluble *	2.23	4.19	7.77
Alkali-soluble .....	10.61*	38.10	65.31
Cellulose .....	58.96	41.66	8.47
Acid Hydrolysis .....	0.71	0.28	0.17
Pentosan .....	7.16	6.79	2.96
Methyl Pentosan .....	2.64	3.56	6.06
Methoxy Group .....	3.94	5.16	7.80
Ether Extract .....	2.71	2.05	2.72
Ash .....	0.15	0.15	0.65

\* Percentages for "Hot-water soluble" are the Total, less the "Cold-water-soluble."

an increase in hot-water-soluble, methoxyl, and methyl pentosans as the wood decays. Lignin was not determined but the authors concluded that it had been largely modified by the decay since certain constituents supposed to be characteristic of the lignin as methoxyl groups and methyl pentosans increased in proportion, while others as pentosans and acetic acid by hydrolysis decreased. Such a conclusion is not justified since even if some of the pentosans are a part of the lignin, only a small portion of the total pentosans may be considered as thus combined and variations might take place entirely within the pentosans *not* in the lignin. It is also readily conceivable that the pentosans in the lignin as well as the acetyl groups might be split off without any considerable modification of the rest of the lignin.

The next work was by Mahood and Cable<sup>4</sup> on ground wood of mixed spruce and balsam, sound and slightly rotted by a mixture of molds and wood-destroying fungi. Much the same kind of changes were found as those reported by Rose and Lisse, although the attack had been less severe than that on the "partially rotted" sample of the latter investigation. Lignin was also determined in these analyses and it was found to increase with decay as explained in the next paragraph.

It was not until the work of Bray and Andrews appeared<sup>5</sup> that any data were available on the loss of weight and change in chemical composition on the same piece of wood so that the actual percentage loss of each constituent could be determined. Previously the percentage of each constituent based on the sound wood could be compared with the percentage based only on the decayed wood so that a direct comparison could not be obtained. In many cases, for instance, the percentage of lignin was higher in the decayed wood than in the sound, although obviously the actual amount of lignin had not increased during decay.

<sup>4</sup> *Paper*, 25, 1149 (1920).

<sup>5</sup> *Ind. Eng. Chem.*, 16, 137 (1924).

The previous work had also been done largely on wood rotted by mixtures of unknown species of fungi, while these authors used wood which had been inoculated with pure cultures mostly of known species. The changes in composition and the loss of weight due to decay are shown in Table LII. The percentage figures for the different constituents are all based on the weight of the original sound wood. Here again increases are found in the cold- and hot-water-soluble, and in the alkali-soluble constituents and decreases in the cellulose. The lignin remains fairly constant or decreases slightly, the small increases being almost within the limit of error of the determination. In one case where the loss of lignin was 3 per cent, this was found to be almost exactly accounted for by loss in methoxyl and this may also account for other smaller losses in lignin. In one case also where the loss of cellulose was 54 per cent, the loss of pentosan was determined and found to be 9.5 per cent.

In a later paper Bray<sup>6</sup> calls attention to the relation between the increase in alkali-soluble material and the decrease in cellulose and shows that by using an empirical curve the fairly rapid and simple determination of alkali-soluble material may indicate quite closely the loss of cellulose. This relation is close only in the case of the decay caused by the "brown rots."

TABLE LII  
ANALYSIS OF GROUNDWOOD BASED ON EQUAL WEIGHTS OF ORIGINAL SAMPLE  
(Figures in per cent)

Sample	Organism or Culture No.	Loss Due to Decay	Cold-water-soluble	Hot-water-soluble	1 Per Cent Alkali-soluble	Lignin	Cross and Cellulose	Bevan	$\alpha$ -Cellulose	$\beta$ -Cellulose	$\gamma$ -Cellulose
2544	Original Wood (no decay)	0	0.0	1.2	10.1	29.7	60.0	36.3	14.7	9.0	
100	4620-2	27.12	8.1	13.1	40.0	27.7	26.8	5.1	18.0	3.5	
102	4620-2	49.5	7.5	11.1	33.4	26.7	10.9	...	...	...	
182	4620-2	62.4	...	6.2	26.3	26.7	6.05				
130	Fomes roseus	10.3	2.9	5.7	29.6	30.6	44.3	22.0	17.2	5.1	
131	Fomes roseus	12.94	3.2	4.9	29.2	30.3	43.8	...	...	...	
157	Lentinus lepideus	21.54	7.5	11.8	41.0	28.8	32.1	16.5	12.0	3.5	
158	Lentinus lepideus	30.31	9.7	15.7	40.6	28.6	25.8	...	...	...	
106	4620-1	22.2	10.8	13.7	40.8	30.7	29.0	6.9	19.8	2.3	
107	4620-1	33.11	11.1	15.3	41.6	28.8	18.2	...	...	...	
108	4620-1	38.63	9.3	13.0	38.0	28.5	16.9				
148	Peniophora tabacina	13.5	4.8	9.0	34.9	27.7	40.5	22.5	13.9	4.2	

\**Paper Trade Journal*, 78, 58 (1924).

In recent work<sup>7</sup> it has been shown that there is one fungus *Trametes pini*, which attacks the lignin perhaps even more rapidly than the cellulose. This fact had previously been mentioned by Johnsen and Lee<sup>8</sup> who stated that this organism might reduce the lignin by as much as 30 per cent and increase the cellulose by 15 per cent. These percentages are probably based on lignin and cellulose in the original wood, the apparent increase in cellulose being due to a much more rapid attack on the lignin. Unfortunately, we do not have any determinations of lignin in wood where the loss in weight due to the attack of this organism has been determined except in cases where the loss was only a few per cent so that it cannot be surely decided whether the apparently selective attack on the lignin would continue. *Trametes pini* belongs to the class of "white rots" which are supposed to attack the lignin largely and leave the cellulose unchanged, but cellulose determinations<sup>9</sup> on samples of white spruce wood subjected to the action of *Polyporus hirsutus*, another white rot, showed decreases in cellulose content of 12.2, 12.4, and 14.7 per cent where the loss in weight due to decay had been 9.8, 11.2, and 17.4 per cent respectively, so that it cannot be a general rule that the white rots do not attack the cellulose seriously.

It is noticeable in Table LII that the total loss in weight due to decay is usually less than the loss in cellulose, showing that the cellulose is not consumed as such by the fungus, but is first modified into some solid materials which remain, at least temporarily, in the decayed wood. Evidently these are the materials which cause at least a part of the increase in the hot- and cold-water-soluble and the alkali-soluble constituents. We have no further information on the composition of these intermediate products except that they are soluble in water and one per cent caustic soda. It is also interesting to note that there has apparently been a modification of the lignin or the cellulose, or both, so that these substances as present in the partly decayed wood have properties different from those of the lignin and cellulose in the sound wood. This is shown by the fact that in the original wood the sum of the lignin, cellulose, and alkali-soluble is close to 100 per cent while in the decayed wood the sum of these same constituents is always greater than 100 per cent, reaching as high as 157 per cent in the case of sample 182 in which there had been a loss of weight of 62 per cent due to decay. It is noticeable also that there is a fairly close relation between the loss in weight and the sum of those three constituents.

That a part of this increase in alkali-soluble constituent is due to

a modification of the cellulose is indicated by Bray's figures on alpha-, beta-, and gamma-cellulose in Table LII which show that there is a loss in alpha-cellulose and a gain in beta-cellulose due to decay. But this is not sufficient to explain all of the increase in alkali soluble constituents. In sample 182 the decayed wood is soluble in one per cent alkali to the extent of 70 per cent and yet there is only 16 per cent cellulose in the sample. If all the constituents other than lignin were soluble in alkali, still 41 per cent out of the 71 per cent lignin would have to be alkali soluble in order to make up the rest of the 70 per cent which is alkali soluble. The lignin is, therefore, modified by the decay to the extent of rendering it more readily soluble in alkali than the lignin in the original wood. This modification might be a change in chemical composition or even an increase of surface with corresponding increase of solubility.

Another set of analyses of sound and decayed wood in which other constituents were determined<sup>10</sup> throws some further light on the course of decay in wood. This work was done on apple wood infected with *Polystictus versicolor* and the actual loss in weight due to decay was not determined, but by determining the specific gravity of the sound and rotted wood, it was possible to figure the results of the analysis of the rotted wood on the basis of the original sound wood. In these analyses, starch, alcohol-soluble sugars, alcohol-soluble non-sugars, hemicellulose hexosans, and hemicellulose pentosans were determined, the last two constituents making up the sugars formed by hydrolyzing the starch- and extract-free wood with one per cent HCl for three hours. The cellulose was determined on the sample from which the hemicelluloses had been removed. Following are the percentages of the different constituents removed by decay:

Cellulose	{pentosan-free . . . . .	34	Per Cent
	{pentosan-in . . . . .	59	" "
Hemicellulose	{hexosans . . . . .	52	" "
	{pentosans . . . . .	40	" "
Starch . . . . .		18	" "
Alcohol-soluble	{sugars . . . . .	31	" "
	{non-sugars . . . . .	84	" "

These results correspond well with those of Hawley, Fleck and Richards<sup>11</sup> in that the readily hydrolyzed portions of the Cross and Bevan cellulose are more rapidly attacked than the more stable cellulose (corresponding to the pentosan-free cellulose here). It is difficult, however, to explain the lesser attack on the hemicellulose pentosans than on

<sup>10</sup>R. G. Smith, *Phytopathology*, 14, 114 (1924).

<sup>11</sup>Loc. cit.

the pentosans in the cellulose. It is also of interest to note that the starch and the sugars are the two constituents least attacked, although it is generally believed that these are the first attacked and that the durability of a wood is largely determined by the amount of these substances present.

It is probable that the fungus does not directly assimilate the wood constituents and transform them into water and carbon dioxide but that there are present at all times certain intermediate products which may or may not affect the chemical analysis of the decayed wood. This has been indicated by the considerable effect on the physical and chemical properties of the wood while the loss in weight is still slight. When analyzing a complex material like wood and determining mainly aggregates which are in themselves complex, it is possible to have important changes in composition without affecting the analysis to any great extent. It is certain for instance that the cellulose aggregate as isolated from a decayed wood is of different composition from the cellulose from the sound wood, and it is probable that the lignin aggregate is also different. In the same way it is possible that all of the hemicelluloses, the sugars, the pentosans, and even the starch as determined in decayed wood are not constituents of the original wood but that they are hemicelluloses, sugars, etc., formed by the fungus in its primary attack on wood, or more likely, they are not hemicelluloses, sugars, etc., at all, but some intermediate compounds of similar properties which respond in the same way to the analytical methods used.

The attempt has been made to attribute a part of the great increase of alkali-soluble constituents to a modification of the alkali solubility of the cellulose and lignin, but it is not easy to accept this explanation for all the alkali-soluble constituents of decayed wood. It is more difficult, even impossible, to account for the high water-soluble content of decayed wood in the same way, since water-soluble lignin and cellulose are more difficult of conception. The water-soluble constituents of decayed wood must, therefore, be largely intermediate compounds in the final destruction of the wood and yet they may give the reactions for hemicelluloses, sugars, pentosans, or starch. Until there is more detailed analytical work on decayed wood, probably by methods yet to be developed, it is useless to speculate further on these intermediate compounds.

#### The Action of Molds on Wood

Besides the true wood-destroying fungi which cause what is commonly called the decay of wood, there is another class of fungi called the molds which grow on wood under certain conditions. The chemical action of these molds has been studied only in connection with the deterioration of ground wood pulp during storage and apparently molds are not of

much importance in their effect on the chemical composition of solid pieces of wood such as boards and timbers. Although molds may cause serious discoloration of ground wood pulp, yet they do not cause much change in the chemical composition.

In a study of 46 samples of ground wood pulp attacked by 19 species of molds for 6 to 12 months it was found<sup>12</sup> that the maximum loss in weight of the wood was only 1.9 per cent. As in the case of the decay caused by the true wood-destroying fungi this total loss in weight is not so great as the loss in weight of a single constituent of the wood, the cellulose, showing that intermediate products are first formed from the cellulose which remain in the molded wood. In fact the attack of the molds is in general like the beginning of decay in that the water-soluble and alkali-soluble constituents are increased, the cellulose is decreased, and the lignin is little affected.

The greatest increase in alkali-soluble materials due to molding was from a figure of 10.1 per cent in the original sound pulp to 16.5 per cent in the molded pulp and the greatest decrease in cellulose was from 60.0 per cent to 55.4 per cent.

#### Sap Stain or Blue Stain

This is a fungus attack on certain species of wood, especially the southern pines and hardwoods which as the name implies, is restricted to the sapwood. Although it decreases the value of the wood due to its marked discoloration, yet it does not materially affect the strength of the wood and it therefore cannot affect the chemical composition of the structural part of the wood. There are no chemical analyses of sap-stained wood to show just what the effect has been but since the strength is not affected and since the organism must find some food in the wood, it is commonly assumed that the sapwood extractives are the only constituents attacked. Some chemical analyses of sapwood before and after blue-staining would be very interesting and possibly important.

#### Destruction of Wood by the Teredo

The teredo (*Teredo navalis*) or shipworm is a mollusk which lives in wood submerged in salt water. It bores holes throughout the wood until only a honeycomb structure may be left. Although it was long known that the borings passed through the digestive system of the mollusk, it was not until the work of Dore and Miller<sup>13</sup> that there was conclusive evidence of a change in chemical composition of the wood and of a utilization of a part of the wood as food. From the practical

standpoint the attacks of the teredo and fungi are similar since both cause the destruction of important structural timbers. The visible effect of teredo attack is, however, the actual mechanical removal of wood substance.

TABLE LIII  
ANALYSES OF WOOD DIGESTED BY TEREDO NAVALIS  
(Original data recalculated to percentages of original wood assuming lignin unchanged)

Determination	Series I			Series II	
	Wood	Borings (1)	Borings (2)	Wood	Borings
Hemicelluloses .....	6.02	3.62	5.10	14.23	6.20
Cellulose .....	54.74	11.79	10.99	47.45	10.96
Lignin .....	30.60	30.60	30.60	27.84	27.84
Furfural yield .....	5.37	3.32	3.22	5.90	4.26

As might be expected from the analogy with fungus attack, the cellulose is apparently the constituent most rapidly decomposed. It was, of course, impossible to determine the actual loss in weight of the wood during the digesting process, but by assuming that the lignin was not changed in amount, it was possible to calculate the analyses thus calculated. The hemicelluloses were determined by hydrolysis of the alcohol-extracted wood with one per cent HCl for three hours on the steam bath, and the cellulose and lignin were determined on the residue from this hydrolysis. It is noticeable in these figures that although the cellulose has been largely decomposed, there are yet considerable residues of hemicelluloses and pentosans still present as in the case of decayed wood. It is not so likely in this case that some of the materials determined as "hemicelluloses" are intermediate products in the decomposition of the cellulose since the substance analyzed is a final product of digestion and the intermediate products should have been completely transformed and assimilated.

#### The Destruction of Wood by Termites

Termites, sometimes called "white ants," are responsible for the serious destruction of wood in tropical and semi-tropical countries. The wood seems to be their principal article of diet and the undigested residue is used in building their nests. Analyses of the original wood and the nests with correction for ash and moisture show much the same results<sup>14</sup> as in the case of the teredo. The cellulose is reduced from 54.6 per cent to 18.0 per cent and the pentosans from 18.0 per cent to 8.5 per cent during digestion. Lignin and alkali-soluble determinations were not made

<sup>14</sup> M. Oshima, *Philippine J. Sci.*, 15, 340 (1919).

and there was no chance to determine the loss in weight of the wood. Here again the cellulose is the most readily assimilated part of the wood and the pentosans are apparently not attacked as rapidly as the other polysaccharides.

### The Deterioration of Wood by Chemicals

The different kinds of deterioration of wood so far described have been due to natural agencies such as various forms of plant and animal life. There is, however, an important deterioration which takes place under artificial conditions when wood is used in contact with chemicals.

In previous chapters various decompositions by heat and chemicals have been described in detail but no special discussion has been given of such decomposition as might result from the action of various chemicals in contact with wooden tanks, pipes, or other chemical apparatus. There are no data on the changes in chemical composition due to such action and it is difficult to draw any definite conclusions by analogy with the more drastic decompositions already described. The conditions are very different in that the chemical reagent is commonly more dilute, or the temperature lower, or the time much longer. Of course, we would expect the same kind of a reaction under these less severe conditions, but there is no way of telling how long it would continue or how far it would progress. For instance in a tank containing a cold 5 per cent HCl solution we might expect a slow hydrolysis, but we could not tell by analogy with the high temperature hydrolysis how much of the polysaccharides in the wood might be hydrolyzed and dissolved in a given time.

The cold-water-soluble constituents would be rapidly dissolved wherever the solution could come in contact with them but the solution and removal of these constituents except from that part of the wood next to the inside surface of the tank would be very slow. The removal of extraneous matter would hardly be classed as deterioration of the wood but it might be important in contaminating the contents of the tank. The main interest in the deterioration of wood by chemicals lies not so much in the chemical changes of the wood as in the resistance of different species to chemical action and this subject will be taken up later in that part of the chapter dealing with the natural durability of wood.

### The Natural Durability of Wood

Certain species of wood such as cypress, redwood, locust, catalpa, the white oaks, the cedars, and certain pines are known as durable woods in contrast with other species which are readily infected and decay rapidly. The sapwood of all species is also more susceptible to decay

than the heartwood, except in the case of those species whose heartwood is practically non-resistant to decay. Except for the extraneous materials there is not sufficient difference in the chemical composition of various species or of heart and sap to account for these differences in resistance to decay, so that differences in durability, of heart and sap at least, have been ascribed to the extractives. It has commonly been assumed that the presence of certain soluble and easily assimilated substances in the sapwood such as "sugars, starches, gums, etc., " acted as promoters or accelerators of decay by furnishing a ready food for the fungus while the absence of such substances in the heartwood made it difficult for the fungus to get a start. Such a theory, however, failed to account for the fact that in certain species of wood the heartwood decayed almost as readily as the sapwood.

It seemed more reasonable that durability was due to the presence of toxic substances rather than to the absence of accelerators since this conception made it unnecessary to assume the presence of extractives in the heartwood of non-durable species similar to the special accelerators of the sapwood. This conception also agreed with the facts that the especially durable species contained, in heartwood but not in sapwood, extractives of peculiar characteristics which might account for the durability. The durability of certain species had been ascribed to the presence of such extractives but it was not until the work of Hawley, Fleck, and Richards<sup>15</sup> that several durable and non-durable species were studied from this standpoint and the general subject developed experimentally.

The authors extracted the hot- and cold-water-soluble constituents from heartwood and sapwood of several species and determined the toxicity of the extracts for a wood-destroying fungus. Briefly, it was found that the hot-water extract was always more toxic than the cold-water extract and that the heartwood extracts were always more toxic than the sapwood extracts. In general the toxicity of the extracts was about what would be expected from the durability of the wood, although there are no figures for natural durability from which accurate comparisons could be made. Red oak was the only exception to this general relationship between toxicity of extract and durability of wood.

It is a common opinion, based on experience, that the white oaks are considerably more durable than the red oaks, in fact the white oaks are classed as durable and the red oaks as non-durable. Yet the red oak and white oak cold-water extracts from the heartwood had about the same toxicity and the red oak hot-water extract was 76 per cent as toxic as the white oak. This exception can be explained only on a basis of the permanence of the toxic extracts. It is well known that

red oak is much more readily permeable to liquids than white oak and under the conditions where durability is tested the red oak extracts may be rapidly removed by leaching, while the white oak extracts may remain for a long time in sufficient concentration to prevent decay.

This experimental work was limited to durable species which were known to contain considerable quantities of water-soluble tannins or coloring matters and similar tests on durable woods containing oils and resins are yet to be made. Meanwhile, however, Bateman<sup>16</sup> has shown that in the case of one durable species containing a resin, the toxicity of a part of the resin is sufficient to explain the durability of the wood. He found that a certain longleaf pine railroad tie, which had been in service fifteen years without decay contained no zinc chloride, although it was supposed to have been treated with this preservative. The wood was distilled with steam to remove the volatile constituents of the resin, the turpentine and pine oil, and the toxicity of the oil was determined. It was found that even after long service the tie contained much more toxic oil than was necessary to prevent decay. It is probable that similar results will be obtained in testing other durable woods containing resins or oils.

This subject of natural durability of woods cannot be dismissed without referring to the work of Zeller<sup>17</sup> who after obtaining a large amount of experimental data concluded that there was no relationship between the resin content and durability of different samples of longleaf pine, except possibly in the case of samples containing 18 per cent or more of resin. His method of attacking the problem was by inoculating samples of wood of different resin content with fungi and measuring the amount of decay by the loss in weight. His figures showed no relation between resin content and loss in weight, but there were several chances for error in his method.

The sterilization of the samples previous to inoculation was carried out under just the proper conditions for removing a large part of the volatile oil (which Bateman has since shown to be the main toxic part of the resin) and therefore the sterilized wood was not comparable with the natural wood in its resistance to decay. Another mistake in manipulation was made when several different samples with different resin contents were put in the same culture jar for observing the effect of decay. Since the natural preservative in the wood was volatile the presence of specimens with considerable resin may have affected the growth of the fungus on the less resinous specimens.

In a previous paper Zeller reported that fungi could grow on agar containing 50 per cent resin but he made the common mistake of using

<sup>16</sup> *Southern Lumberman*, 115, 51 (1924).

<sup>17</sup> *Ann. Missouri Botan. Gardens*, 4, 93 (1917).

*rosin* and calling it *resin*. In this case the difference between rosin and resin lies in the presence of just those toxic oils which render the resin a natural preservative. Altogether there were so many chances for error in Zeller's work that his conclusions cannot be accepted, especially in view of Bateman's evidence that the oils which may remain in longleaf pine wood for a long time under service conditions are very toxic to wood-destroying fungi.

There are few experimental data on the natural resistance of different species of wood to the action of various chemicals when used for tanks, pipes, and other chemical apparatus. There is, however, considerable general information on the subject obtained from the experience of the manufacturers and users of wooden tanks. The list of woods commonly used for such purposes sound much like a list of woods resistant to decay—longleaf pine, Norway pine, white pine, Douglas fir, Western red cedar, cypress, redwood, oak. This similarity between resistance to decay and to chemical action naturally leads to the conclusions that unusual resistance to chemical action is also due to the extraneous materials in the wood. There may be no direct evidence but the indirect evidence is largely in one direction. Aside from the indirect evidence just given, there is the fact that we know of no variations in chemical composition (aside from these due to extraneous substances) which would tend to make one wood more resistant than another to chemical attack.

The mechanism of the protection against the attack of chemicals is probably different from that of protection against decay. We have seen that resistance of wood to decay is due largely to the toxic action of certain extraneous materials on the fungus but it is difficult to conceive that the extraneous material acts as a "poison" or negative catalyst of, for instance, the hydrolysis of wood by dilute acids in the cold. It seems more likely that the extraneous material, itself resistant to the action of the chemical, furnishes a mechanical protection for the wood. This conception is not difficult to follow in the case of the protection offered by resinous materials against the action of acids but it does not explain so readily the apparent protection by materials soluble in dilute acids against the action of dilute acids. We do not have sufficient data on the specific resistance of woods with known composition of extraneous materials against certain chemicals to make further speculation of this kind profitable.

The only experimental work on this subject is that of Hauser and Bahlman.<sup>16</sup> They compared six species of wood commonly used in contact with chemicals, cypress, Douglas fir, longleaf pine, redwood, hard maple and white oak. These woods were subjected to the action of various concentrations of hot and cold hydrochloric, sulfuric, and nitric acids and caustic soda. No quantitative measurements of loss in strength or in weight

<sup>16</sup> *Chem. Met. Eng.*, 28, 159 (1923).

were attempted but the general appearance and properties of the wood samples were noted after treatment for the same length of time. In general the effects of nitric acid and caustic soda were most severe followed by the sulfuric and hydrochloric acids. The wood which seemed best to withstand the action of the solutions was longleaf pine followed in order by cypress, Douglas fir, maple, oak, and redwood.

These results are somewhat at variance with the common opinion that redwood is very resistant to acids and alkalies and that oak is more resistant than maple. From the standpoint of the protective effect of extraneous materials in the wood it would be expected that maple would be the least resistant of these species and that redwood would be at least as resistant as Douglas fir. If we assume that the resistance is due to extraneous materials it is possible to explain these unusual results. It is known that the amount of extraneous materials may vary widely in different samples of wood from the same species and possibly the amount of resins in the pine, cypress and fir were unusually high and the tannins and coloring matter in the oak and redwood samples were unusually low. This, however, does not offer any explanations for the good showing of the maple which does not contain any protective material. Apparently maple is resistant on account of some unknown chemical or physical property.

More experimental work is desirable on this subject with quantitative determinations of the effect of the chemicals and with known amounts of extraneous materials in the samples of wood used.

Oshima<sup>19</sup> has shown that certain woods like teak and cypress pine immune to the attack of termites contain unusual quantities of benzene extract and the volatile oil from the cypress pine when injected into Japanese pine (a non-resistant wood) prevented the attack of the termites. Other woods strongly resistant to termites did not contain much benzene soluble material but no attempt was made to show whether water-soluble constituents might not have been responsible for the resistance.

Certain woods such as greenheart, resistant to the attack of the teredo, are known to contain unusual quantities of extraneous material but no experimental work has been done to prove that these account for the durability.

#### Effect of Decay on Value of Wood for Industrial Chemical Processes

- With the information at hand on the effect of decay on chemical composition and on the relation between chemical composition and value for chemical processes it is now possible to speculate a little on the effect of

<sup>19</sup> *Loc. cit.*

using partly-decayed wood in such chemical processes as pulp making and distillation. In the case of pulp making by the chemical processes it is not so necessary to speculate since some actual experimental data are available and it is only necessary to correlate the data.

Rue, Miller, and Humphrey<sup>20</sup> have made sulfite cooks on decayed wood of known chemical composition with the results shown in Table LIV. These figures show that several samples of decayed wood although they contain less cellulose than sound, yet give nearly as high or even higher yields of pulp. This can be explained only by correlation of the data previously presented showing that (1) the pulp yields from wood correspond to the more stable part of the cellulose (p. 238) and (2) the decay of wood results in the more rapid removal of the less stable cellulose constituents (p. 300). The crude cellulose from partly-decayed wood may therefore contain a higher proportion of stable cellulose than that from sound wood—enough higher to counterbalance the smaller percentage of crude cellulose in the wood.

TABLE LIV  
CHEMICAL PROPERTIES OF PARTLY DECAYED PULP WOODS

The samples for each species are listed in order of decreasing firmness of wood

Sample	No.	Fungus	Solubility in 1				Yield of Screened Pulp	
			Volume of Discolored Wood	Per Cent Sodium Hydroxide	Per Cent Lignin	Per Cent Cellulose		
<i>BALSAM</i>								
975-0	None		None	9.3	30.7	57.1	49.6	
975-3	"Hemlock heart rot", grade 1		55	13.6	31.8	53.9	51.0	
975-4	"Hemlock heart rot", grade 2		74	14.1	30.8	53.9	48.9	
975-1	Mixed feather rots		31	11.9	31.8	54.8	50.6	
975-6	<i>Polystictus abietinus</i>		66	13.3	30.0	54.0	49.1	
975-5	"Hemlock heart rot", grade 3		100	17.6	28.7	53.5	45.6	
975-2	<i>Fomes pinicola</i>		69	20.6	34.5	49.7	40.0	
<i>SPRUCE</i>								
963	None		None	10.4	28.4	58.4	45.7	
975-7	<i>Trametes pini</i>		96	15.6	25.8	59.8	51.1	

Where the decay has progressed further (to a point where the alkali solubility is 17.6 per cent in comparison with 9.3 per cent in the sound wood) even the stable cellulose has been attacked and the yield of pulp may be decreased. It is noticeable that the first five samples of decayed wood contain very nearly the same percentage cellulose, and yet the yields of pulp vary from 45.6 per cent to 51 per cent. This indicates a considerable

<sup>20</sup> *Pulp Paper Mag. Can.*, 22, 93 (1924).

variation in the composition of the material determined as crude cellulose in the analyses of these woods.

In the case of the spruce wood attacked by *Trametes pini*, the percentage of cellulose in the decayed wood is actually higher than in the sound wood showing, as has been previously mentioned, that this fungus may attack the lignin even more rapidly than the cellulose. The slightly higher cellulose content of the decayed wood (only 1.4 per cent) is, however, not sufficient to explain all of the considerably higher yield of pulp (5.4 per cent) and again the smaller proportion of unstable cellulose in the decayed wood must be used to explain the rest of the increase.

The beginning of decay in wood is similar to the pulping process in that the lignin or the more easily hydrolyzed portions of the cellulose, or both, are removed and the yields of pulp are, therefore, not reduced. In some cases where the lignin has been removed to a considerable extent the yields of pulp per unit weight of wood may be even increased.

The effect of decay on the value of wood to be used in a destructive distillation process for the production of methanol and acetic acid has not been determined by any experimental work. It is also difficult to come to any definite conclusions on this subject by theorizing since we do not know enough details about the sources of the distillation products among the components of the wood. In the case of the methanol it has been shown, in Chapter 2, Part IV, that it comes from a part of the methoxyl groups in the lignin and it has been shown in the discussion of the effect of decay on chemical composition that a part of the methoxyl groups in the lignin may be removed during decay, but we do not know whether these two parts of the methoxyl groups are identical. It has been suggested by Ritter (see p. 206) that the methoxyl removed during the isolation of lignin for analytical purposes corresponds to the methanol formed by destructive distillation and it would be a reasonable assumption that this methoxyl also corresponded to the methoxyl removed during decay, each being that portion most readily removed by hydrolytic processes. If these assumptions were true, there would be less methanol obtained by distillation of decayed wood than of sound wood.

There is a little experimental evidence (p. 205) that the pentosans are the source of much of the acetic acid obtained by the destructive distillation of wood and it has been shown that a part of the pentosans are removed during the decay of wood, but here again we do not know whether that particular part of the pentosans removed by decay is identical with the part which is the source of the acetic acid. If the acetyl groups in the original wood are a source of part of the acetic acid this source may be somewhat decreased by decay since Rose and Lisse<sup>21</sup> have shown that in the case of Douglas fir wood the "acetic acid by hydrolysis"

<sup>21</sup> *I. o. c. cit.*

was reduced from 0.71 per cent in sound wood to 0.28 per cent in partly decayed, and 0.17 per cent in completely decayed wood.

On the subject of the effect of decay on the value of wood for hydrolysis by dilute acids, there are also no direct experimental data, but some fairly definite conclusions can be drawn with safety. It has been shown that the more readily hydrolyzed portions of the cellulose are removed by decay more rapidly than the stable part of the cellulose and since the more readily hydrolyzed portions are the main source of the sugars, the sugar yields would be decreased. It is also likely that the proportion of fermentable sugars obtained by hydrolysis of decayed wood would be different, but we do not have enough data on the relative speed of removal of pentosans and hexosans to predict whether there might be more or less fermentable sugars formed. It might be found that some of the ill-defined changes in the residual cellulose due to decay (see p. 299) would make it more readily hydrolyzable and thus increase the sugar yields, but this is only a bare possibility. In the case of hydrolysis by concentrated acids, the decrease in total sugars would be proportional to the decrease in total cellulose due to decay since by this process of hydrolysis practically complete conversion of cellulose into sugar is obtained.



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